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FROSTED PHOTOPLASTIC

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by

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## I. INTRODUCTION

Because of the extreme environmental conditions anticipated in future aerospace reconnaissance, new unconventional recording media are required. These new photographic media must possess high resolution, be radiation-resistant and be capable of rapid, dry processing. Sensitometric properties must be matched to the special needs of reconnaissance missions.

This project sponsored by the Air Force (AF33(657)8814) is directed toward improving electrostatic thermoplastic photography in order to meet the objectives outlined in the Request for Proposal Nr. 33(657)-62-5149-Q. The requested system involves exposure of a photoconductor such that an electrostatic latent image is formed and simultaneously transferred to a thermoplastic film, capable of heat development to create a deformation image.

The preferred technical approach pursued on this contract has been to combine charge transfer through a thin film of "insulating liquid" with development of the electrostatic image by frost-type deformation. The proposed imaging system and methods are shown schematically in Figs. 1 and 2. Effort has also been expended on formulation and evaluation of panchromatic photoreceptors based on multilayer structures involving selenium as a storage layer and a selenium-tellurium alloy as a control layer.

Charge transfer through a thin layer of liquid was selected for this feasibility study rather than transfer of the electrostatic image by air breakdown because prior experience indicated that the former would overcome the problems of high voltage threshold, critical gap spacing, and nonuniformity of transfer associated with air breakdown. Frost development of the transferred electrostatic image was preferred because it provides a thermoplastic imaging method capable of continuous-tone response in the absence of any optical or physical screening of the image. Heat-softening a thin thermoplastic film bearing the electrostatic pattern gives directly a light-scattering deformation image of inherently high resolution continuous-tone quality.

Knowledge gained on a prior Air Force contract at the General Electric Company,<sup>1</sup> on an Air Force-Navy contract at Xerox<sup>2</sup> and on company-sponsored research programs<sup>3,4</sup> served as a starting point for this current project. The over-all program is designed to show laboratory feasibility of a photographic system capable of high resolution, continuous-tone response, a sensitivity equivalent to ASA Exposure Index 10 and spectral response from 4000-8000 angstroms, which is based on thermoplastic imaging and charge transfer.

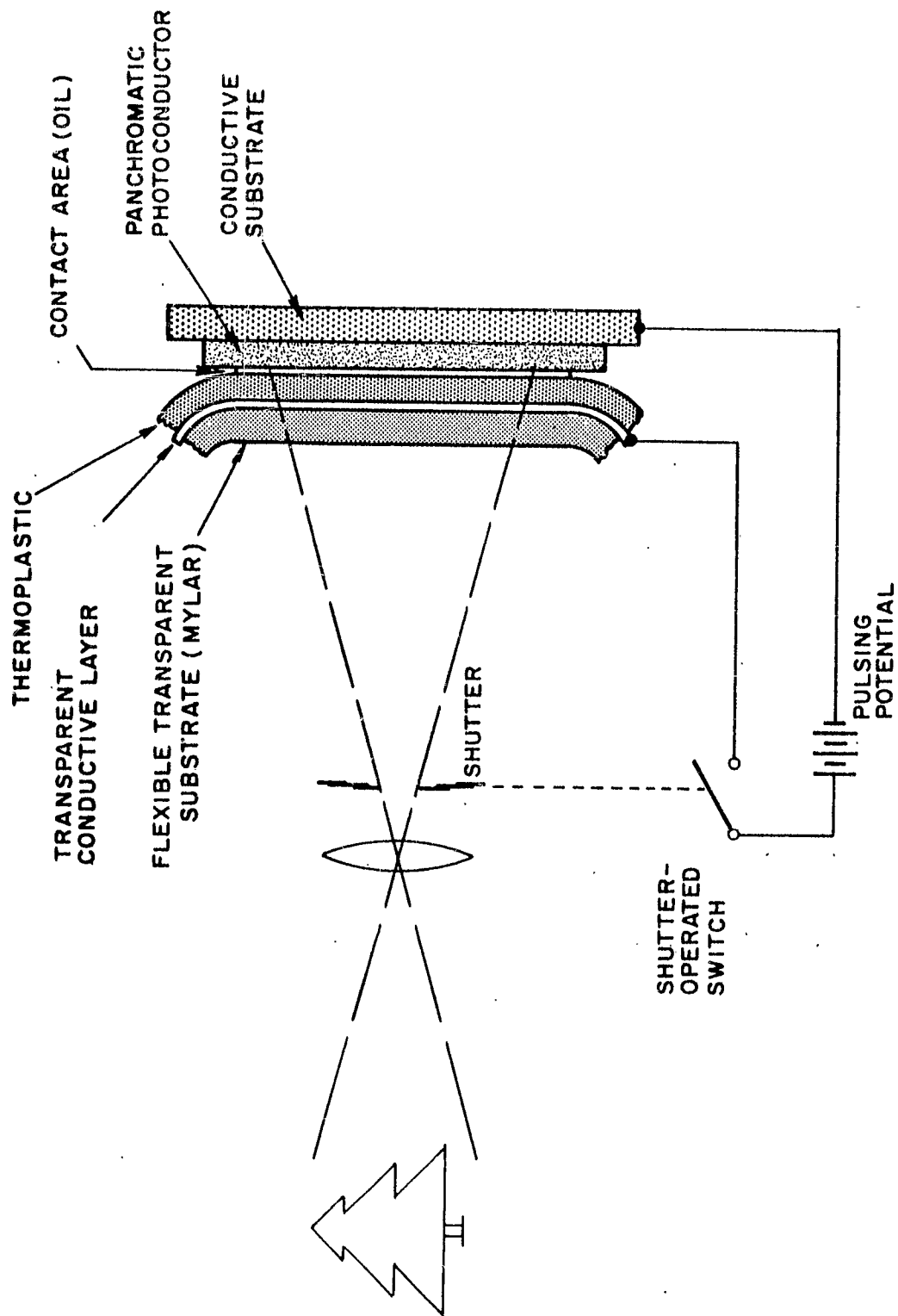


FIGURE 1. Simultaneous Exposure-Charge Transfer Process  
Employing Oil Coupling

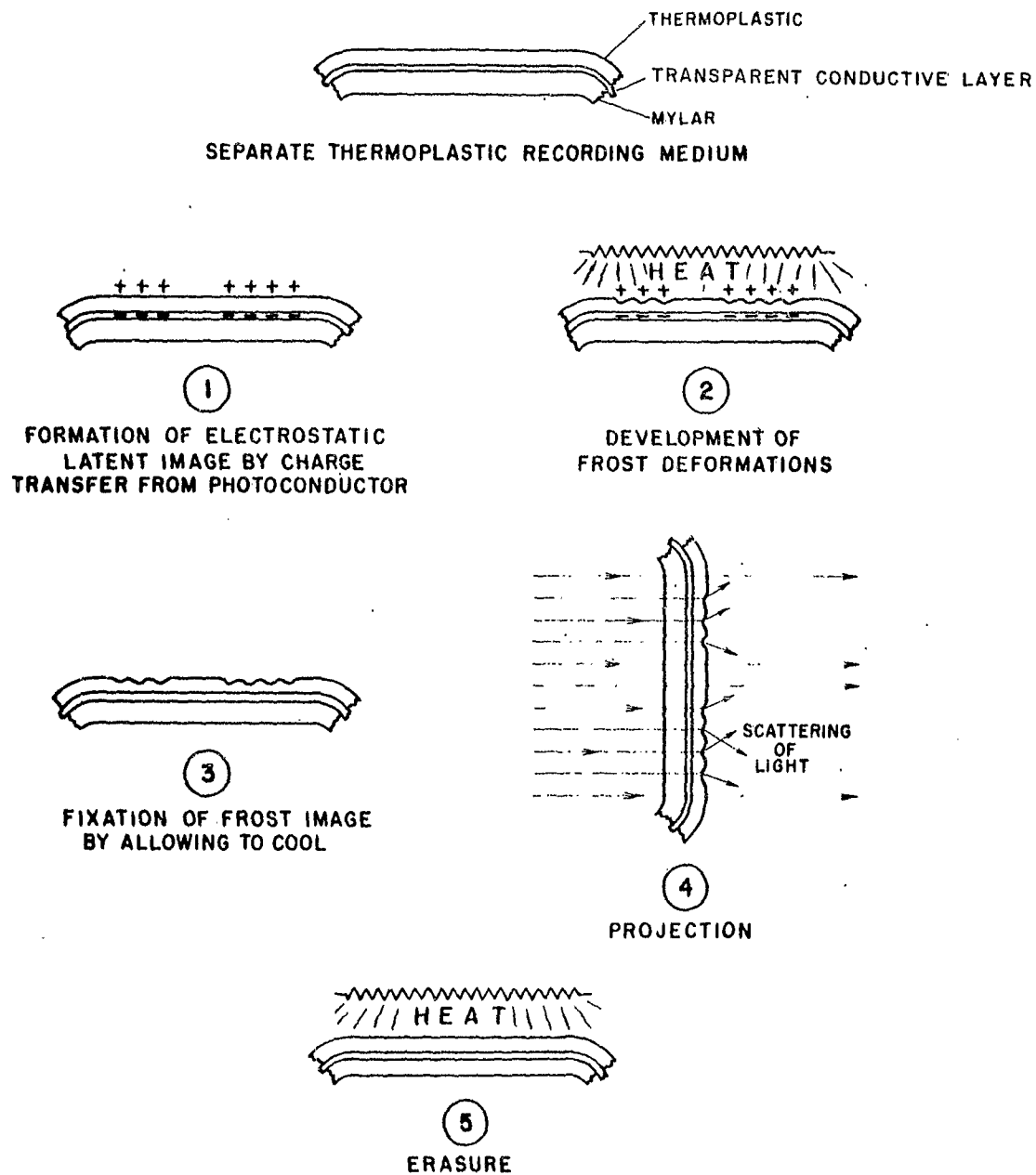


FIGURE 2. Steps in Processing the Thermoplastic Storage Medium

As originally scheduled, this project was to be completed July 31, 1963. This second interim report, however, is written in anticipation of the granting of a 6-month, no-cost contract extension. An extension was applied for to allow time for the redesign of the camera-processor unit, and to make possible more efficient utilization of remaining research funds. These changes in project plans were necessitated by unforeseen problems - particularly those in the charge transfer process and in film manufacturing.

## II. SUMMARY

Estimated cumulative percent progress toward technical objective: 75%

Major accomplishments to date can be summarized as follows:

1. Photoreceptor: The preferred structure is a thin SeTe interface layer on a conductive-glass substrate with a selenium charge-storage overlayer. This plate has shown a resolution capability of 147 lp/mm by xerographic development. Response is roughly panchromatic with efficiency ranging from approximately 60% in the blue-green region of the spectrum to approximately 4% at 8000 Å. Sensitivity to daylight exposure is 3 to 6 times that of conventional selenium plates. In preliminary imaging tests using the charge-transfer/frost system, image defects due to photoconductor non-uniformities were undetectable. Several selenium-tellurium plates with closely similar electrical characteristics have been made.

2. Methods: The effects of a number of variables such as time, temperature, film-thickness, etc. on the characteristics of frost development have been determined in sufficient detail to guide in the design of the camera-developer device and aid in the optimization of its performance.

Extensive studies of the mechanism of charge transfer in liquids have not been possible within the scope of the present project, but practical studies suggest ionic conduction. Liquids compatible with the deformable layer are available in a range of conductivities so that the best compromise can be made between image resolution and completeness of charge transfer. Electrostatic images with resolutions as high as 100 line pairs per millimeter have been created by the charge transfer process, but the highest resolution so far obtained for the complete process

including frost development is 41 line pairs per millimeter. It is expected that this value can be improved in the camera-developer device by reducing the time between transfer of the electrostatic image and frost development.

3. Materials: Two thermoplastic materials have been formulated which seem suitable as the deformable medium to show laboratory feasibility of this frosted photoplastic photographic system. The causes of aging effects on the coated thermoplastic have been elucidated, so that adequate shelf-life for the purposes of this contract is attainable. One material provides frost images that are erasable by heat. Prior to use, the coatings are stable for months. A second material, whose coatings are stable only for periods of weeks, provide frost images that can be permanently "fixed." The relation between chemical structure and these properties is to a large extent now understood.

Two classes of liquids have been found which are suitable for the charge-transfer process. These liquids can be doped with additives to give a range of conductivities. One class of liquids evaporates quickly so that frosted images require no cleaning; the other class does not readily evaporate, but presence of the liquid on the film during development is advantageous in increasing frost sensitivity and development latitude.

4. Camera-Developer Device: An elementary camera-developer device was constructed and has been tested for the production of full-size (2" x 2") images. Because of the requirement for reducing the time interval between film operation and heat development, a revised machine is being designed.

Problems that remain are as follows:

1. Photoreceptor: Plates will require more testing for uniformity and freedom from fatigue as the charge-transfer/frost process is improved, but results at present are very encouraging.

2. Methods: Effort is required to improve the reliability and accuracy of the charge-transfer process while maintaining adequate resolution and efficiency. A decision must be made whether evaporable or non-evaporable charge-transfer liquids will be used. Optimum operating conditions must be established.

3. Materials: Film manufacturing methods must be improved.

4. Camera-Developer Device: The revised camera-developer device must be designed, built and tested.

### III. PHOTORECEPTOR PROGRAM

#### A. TECHNICAL APPROACH

The requirements of this contract specify photoreceptor performance compatible with camera use. The plate must be sensitive to light between 4000 Å and 8000 Å with a daylight ASA Exposure Index of at least 10. The system should approach a resolution in the range of 100 to 200 line pairs per millimeter, implying a plate resolution capability considerably higher, since other elements of the system, such as the optics, tend to degrade the image. Also, the system must be capable of continuous-tone response, which strongly implies a high degree of uniformity of electrical properties over the entire plate. Panchromatic plates, generally, have not possessed high resolution and good uniformity over large areas, based on previous experience.

Since ordinary selenium plates are quite satisfactory for evaluation of other process steps, e.g., charge transfer, the photoreceptor program has, until recently, proceeded quite independently. Two general types of panchromatic plates have been investigated. In the "front" plate, a selenium layer, deposited on a conducting substrate, is coated with a thin selenium-tellurium alloy layer. Light exposure is made from the front. In the "rear" or "interface" plate, the alloy layer is sandwiched between transparent conducting substrate and selenium. Exposure is made from the rear, i.e., through the substrate.

After a number of plates of both types were made and tested, the rear plate was found to have several advantages. Higher resolution could be obtained with it. For comparable dark currents, an alloy of higher tellurium content could be used, resulting in photoresponse to longer wavelength radiation, and somewhat greater daylight response. With rear exposure, control of the optical density of the thermoplastic electrode is unnecessary. In addition there will probably be less mechanical interference with the handling of the thermoplastic electrode in any simple imaging device. One disadvantage of the rear plate is the introduction of optical aberrations by the Pyrex substrate. It appears possible to correct for the most serious of these, spherical aberration and curvature of the field, by repositioning the lens elements of the lens made available by the Air Force for use on this contract. In future work this difficulty might be minimized, for example, by the use of very thin substrates. Because these optical problems are remediable, it was decided to concentrate on the rear plate.

## B. RESOLUTION

Experiments to determine the resolution capability of front and rear SeTe\* plates were described in the first interim report.<sup>5</sup> In order to retain a high resolution electrostatic image, it is necessary for at least one surface of the photoconductor to have high transverse resistivity. When the slightly conducting SeTe alloy is deposited on the front surface of the plate, it permits lateral diffusion of the electrostatic image, resulting in loss of resolution. On the other hand, when the alloy is at the rear, the frost selenium surface retains its ability to hold the electrostatic image. However, as the rear is exposed to an optical image, the electric field lines through the selenium layer depart from their initial direction, normal to the substrate and surface. This occurs in such a way that the charge carriers tend to migrate toward areas corresponding to dark regions of the optical image, eroding away the edges of the electrostatic image. Experiments reported previously indicate that lateral diffusion at the surface is a more serious limitation on resolution than the electric field distortion with rear exposures, although some improvement might be expected with front exposure when the processing times are shortened.

Since the resolution test is essentially a xerographic line-copy technique, only structures with low or moderate dark discharge rates can be evaluated. Plates with higher tellurium content were made which gave improved panchromaticity and daylight speed with dark currents acceptable for the electroded imaging systems. However, their xerographic dark discharge rates were too high to permit satisfactory development of resolution chart images. Brief attempts to develop an image in an electroded configuration were unsuccessful. It was therefore decided to defer further evaluation of resolution until the frost imaging system becomes available for this purpose.

## C. PLATE UNIFORMITY

### 1. General

Plate uniformity includes the problems associated with making, reproducibly, structures with smooth layers of uniform thickness and uniform electrical properties.

### 2. Film Smoothness

Many small irregularities in the plate originate with small pits in the EC\*\* Pyrex substrate left from imperfect polishing. The evaporated films then form a replica of the rough substrate.

\* SeTe = Selenium-Tellurium alloy

\*\* EC = Pyrex glass with electrically conductive layer.

Commercial Pyrex was polished to optical-filter quality by Corning Glass Works, then EC coated. A panchromatic plate made with one of these substrates appeared much smoother than those with commercial grade EC Pyrex. A different type of irregularity was visible on the plate which appeared to result from contaminated solvent used in cleaning the substrate. Experiments now in progress suggest that a variation in the substrate cleaning procedure will eliminate these problems.

In the first tests of a panchromatic plate in the frost imaging system, a commercial EC Pyrex substrate was used. No increase in the number of image nonuniformities could be detected over that obtained with a selenium plate with a smooth brass substrate. However, because charge transfer is presently not completely uniform, these tests must be repeated as the process is improved.

### 3. Thickness Uniformity and Reproducibility

Uniformity of substrate thickness is important because the optical image must be accurately focussed through the Pyrex. Thickness measurements of several random samples showed that the variations within one plate were slightly smaller than with commercial EC Pyrex, although there was somewhat more variation in the average thicknesses from plate to plate.

Reproducibility of SeTe thickness has been improved somewhat. The powdered alloy is dropped into a hot crucible to minimize fractionation from slow evaporation. Uncontrolled amounts of alloy are lost as it bounces out of the crucible. A more enclosed crucible was built which was fed from a water-cooled tube through a hole in its side. At first, the tube, because of its close proximity to the crucible, could not be cooled sufficiently to prevent clogging with powder. A movable vapor shield was then inserted between crucible and tube which reduced but did not reliably prevent clogging. In addition, violent blow-back of the powder was observed, apparently due to the fast vaporization rate. At this point, it was decided to retain the water-cooled tube and revert to the original open crucible. This permits more gentle dropping of the alloy, with less bouncing, although some material is still lost. Although a series of thickness uniformity measurements has not been made, the reproducibility can be deduced indirectly from the consistency of electrical properties of the plates.

### 4. Electrical Uniformity and Reproducibility

In addition to freedom from minor imperfections, the photoreceptor should have consistent electrical properties everywhere within the image area, on each plate. A set of three plates



was made with the following structure: EC + 0.2  $\mu$  40% SeTe + 20  $\mu$  Se. (The percentage is that of the tellurium in the alloy.) Two of the plates had nearly identical daylight response at voltages corresponding to a 10 volts/micron electric field, while the third had about two-thirds of this speed. At lower voltages considerably larger variations were seen but this should be unimportant since our working voltage can be at the high level.

One of these plates was tested for uniformity of photocurrent over a two-inch-square area, through one-square-centimeter electrodes. At the one voltage used, photocurrents varied about  $\pm 10\%$  from the average of five readings.

#### D. SENSITOMETRY

##### 1. General

One of the most important phases of the photoreceptor work has been the determination of optimum composition and thickness of the SeTe layer. As tellurium content of the alloy layer is increased, red sensitivity and dark current increase. At the same time, daylight response reaches a peak, then decreases. We desire the maximum red light sensitivity while retaining high daylight response and acceptable dark currents.

Two general methods have been used to evaluate the electrical properties of various photoreceptor structures: xerographic measurements and cell measurements. These were described in detail in the first interim report.<sup>5</sup> Briefly, in the xerographic test the plate surface is corona charged and its potential measured with an electrometer, both in the dark and in the light. The cell test measures dark current and photocurrent (or charge) with the photoconductor sandwiched between electrodes. A capacitor may be included in the circuit to simulate the thermoplastic electrode.

Xerographic measurements can be made only when dark currents are low enough to permit the plate to hold an electrostatic charge and were not very useful for the evaluation of the present high-tellurium plates. Therefore, sensitometric evaluations were made from cell measurements of charge flow in the dark and in the light. Photocurrents were measured with both white light (daylight response) and monochromatic light (spectral sensitivity). The charge build-up in the simulated thermoplastic electrode was measured as a function of daylight exposure. Optical absorption was also measured for comparison with the spectral data.

## 2. Sensitometric Data

### a. Daylight Response

Photocurrents were measured on several rear structures of varying SeTe composition and thickness. With a -10 volts/micron\* electric field applied, the cell was exposed from the rear with six foot-candles of daylight illumination. The charge passed through the cell in 1/25th of a second (Fig. 3). The structure with a  $0.2 \mu$  40% SeTe interface layer appears to have the optimum daylight sensitivity, although the  $0.1 \mu$  50% SeTe is nearly as fast. Preliminary measurements of a 40% SeTe plate in the camera-developer device, using frost development, indicate that the speed is at least as high as that predicted from these photocurrent measurements (which, roughly, is about 3-6 times that of a conventional selenium plate).

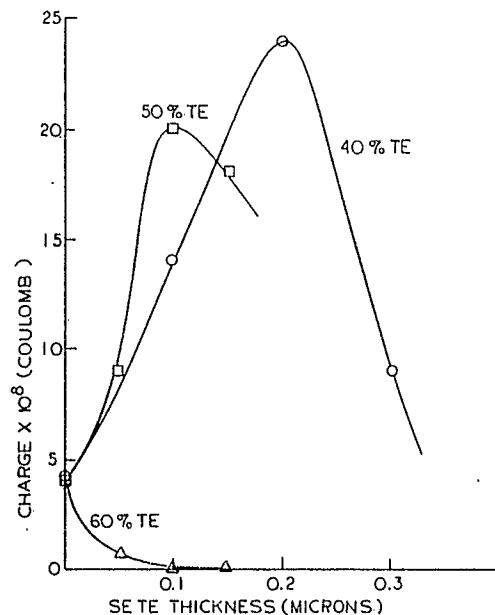


FIGURE 3. Dependence of Daylight Response on SeTe Layer Composition and Thickness

### b. Spectral Sensitivity

The spectral characteristics of these two most sensitive structures were compared to selenium using rear exposure to  $2 \times 10^{12}$  photons/cm<sup>2</sup>-sec. of monochromatic light, with -10 volts/micron applied across the cells. The results are shown in Fig. 4.

\* The minus sign refers to negative polarity on selenium surface.

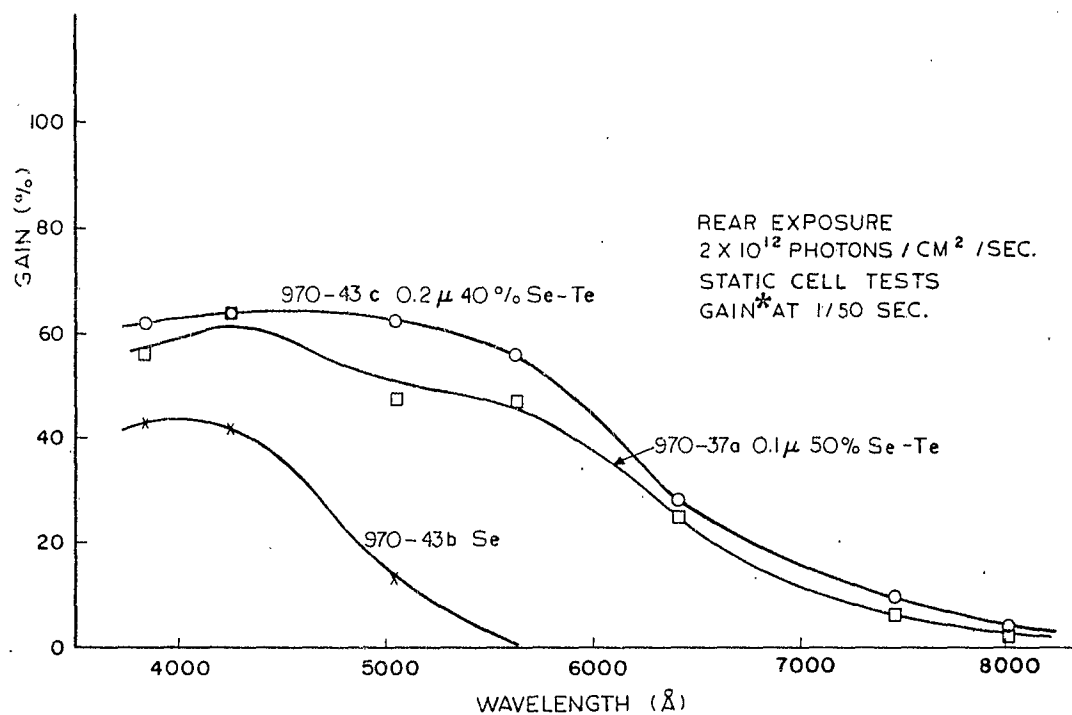


FIGURE 4. Spectral Sensitivity of Rear SeTe Plates

\* Gain is defined as the number of charge carriers traversing the film for each incident photon.

The 40% SeTe structure shows slightly higher sensitivity than the 50%, consistent with its slightly higher daylight response.

c. Photocurrent vs. Voltage Characteristics

The photocurrent measured on panchromatic plates is a strong function of the applied voltage. This is shown in Fig. 5 where the charge passing through the plate in 1/25th of a second is plotted as a function of the applied field. At low fields, an ordinary selenium plate is faster than the panchromatic plates; but, as the field is increased, the panchromatic plate photocurrent rapidly surpasses that of selenium. When a thermoplastic electrode is applied to the photoconductor, the applied voltage is divided between their two capacitances, and as the voltage builds up on the electrode during exposure, the voltage across the photoconductor will be reduced. It is clear from the current voltage characteristics of the panchromatic structures that the voltage cannot be allowed to drop too far or the speed advantage over selenium will be lost.

d. Dependence of Thermoplastic Electrode Voltage on Exposure

A description of the sensitometric characteristics of the process must include the relationship between frost density and exposure. To determine the role of the photoconductor, we need only measure thermoplastic electrode voltage as a function of exposure, since the relationship between frost density and voltage, and its dependence on the method of display, are not directly related to the photoconductor.

The thermoplastic was simulated by a comparable series capacitance. The potential buildup across it was measured as a function of exposure for several values of total applied voltage. This is shown in A of Fig. 6. In a variation of this procedure, designed to more closely match the conditions of frost imaging, the electrode capacitor was precharged to -30 v. to represent the frost threshold potential. The applied voltage was then raised by 30 v. to approximately compensate for the voltage reduction this would cause across the photoconductor. This is shown in B of Fig. 6 which indicates that somewhat more voltage should have been added to properly compensate for the precharge.

For the high applied voltage, an approximately linear relationship was obtained between electrode potential and exposure, so long as the electrode potential was low. Departures from linearity evidently occur when the voltage across the photoconductor is lowered (by an amount equal to the electrode potential) so that the photocurrent is appreciably reduced.

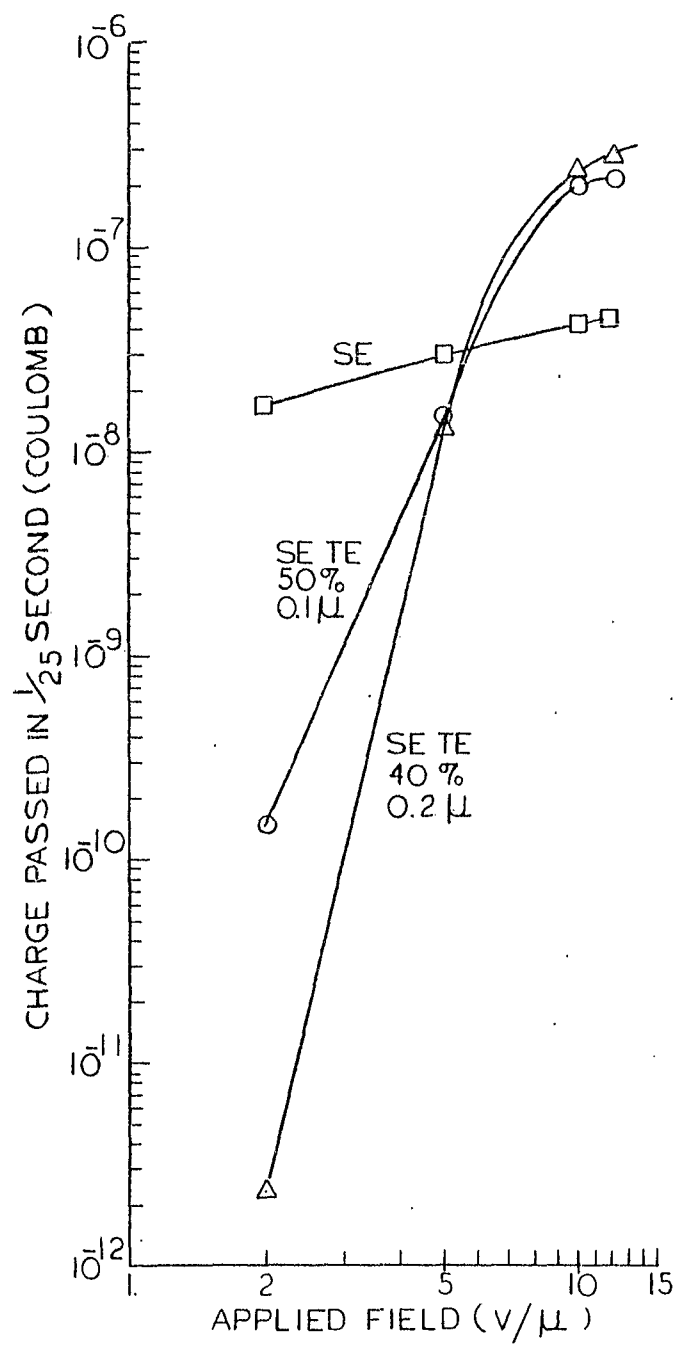


FIGURE 5. Dependence of Daylight Sensitivity on Applied Field

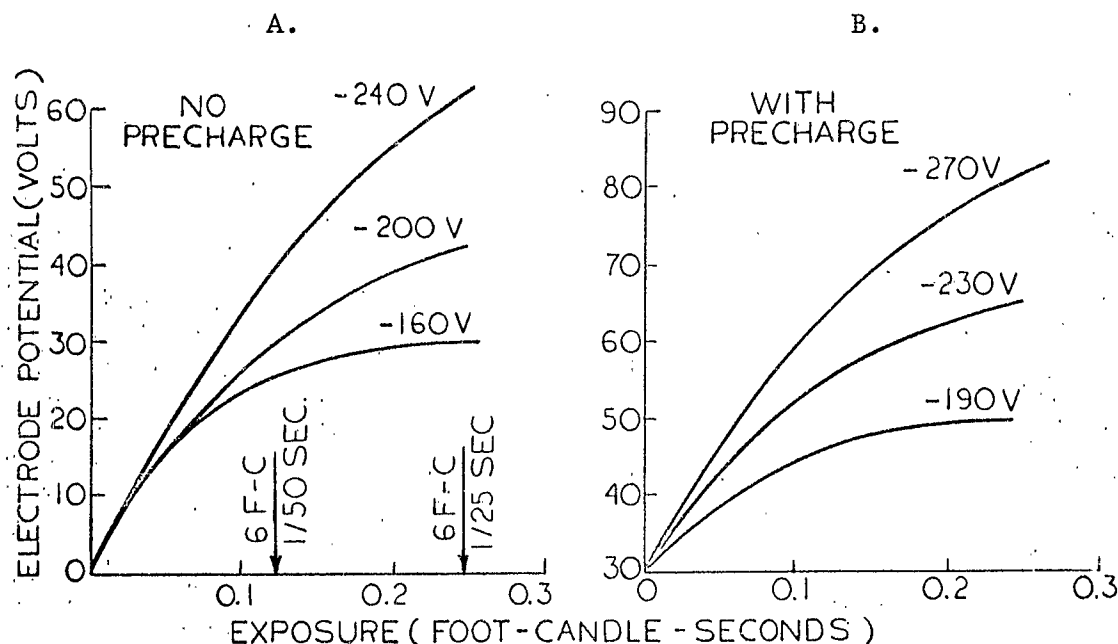


FIGURE 6. Dependence of Electrode Potential on Exposure, With and Without 30 v. Precharge (Curves are shown for different levels of applied potential.)

#### E. OPTICAL ABSORPTION OF SeTe FILMS

For photoconductivity to occur, it is necessary, though not sufficient, for the light to be absorbed in the photosensitive layer. It is instructive therefore to measure the optical absorption of SeTe films in order to estimate the longest wavelengths to which the film could be sensitive. The results of these measurements are shown in Fig. 7 in which the absorption coefficient  $\alpha$  is plotted against wavelength.

The intensity of transmitted light is given by Lambert's law

$$I = I_0 e^{-\alpha d}$$

where an intensity  $I_0$  is incident upon a sample of thickness  $d$ . At 8000 Å it is calculated that a 0.2  $\mu$  layer of 40% SeTe absorbs about 33% of the fraction of the incident light not reflected, while a 0.1  $\mu$  layer of 50% SeTe absorbs about 48%. Thus a

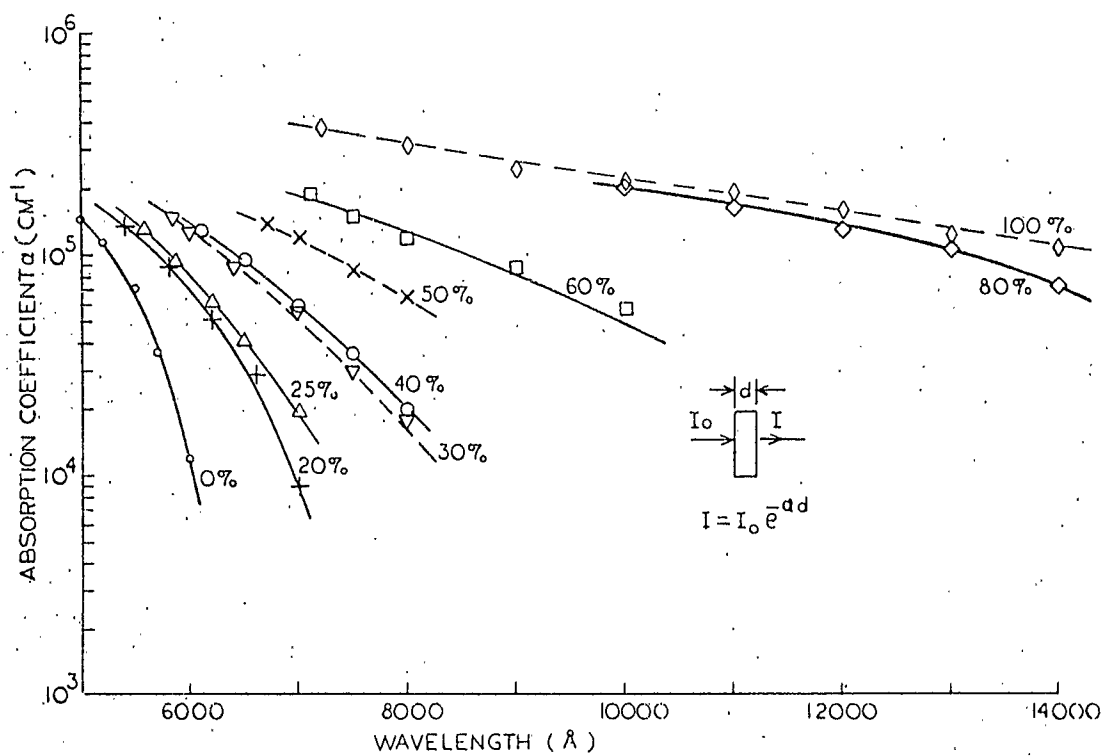


FIGURE 7. Absorption Coefficient of Evaporated SeTe Films

significant fraction of the light is being lost by transmission, but not nearly enough to account for the low spectral response at this wavelength.

## F. FUNDAMENTAL STUDIES

Although the photoreceptor as presently constituted works reasonably well in the imaging system, relatively little is known about the details of the conduction process. A number of single experiments have been performed to try to set up a satisfactory model for the panchromatic structure.

### 1. Film Resistance

The resistance of thin SeTe films on glass was crudely measured by applying ohmmeter probes to the surface. Films with 50% or more tellurium by weight had resistances of the order of a few megohms or less. Films with less than 40% tellurium had resistances too high to measure, > 100 megohms. Two samples with 40% tellurium had widely different resistances, 2 megohms and > 100 megohms.

The relatively low resistance of tellurium-rich films suggests that only a small portion of the external field appears across the SeTe layer, while most of the field is across the selenium. In the simplest model, carriers thermally generated in the SeTe move to the SeTe-Se junction so that many electric field lines terminate on the charges at this junction rather than at the substrate.

### 2. Conductivity Type

If conducting probes at different temperatures are applied to a semiconductor, a voltage will be generated, just as in the Seebeck effect with the more familiar thermocouple. The polarity of the voltage indicates whether the sample is n-type or p-type. This technique was used with the same SeTe films used for resistance measurements. Films with 50% or more tellurium by weight appear to be p-type. One sample of 40% Te was p-type. The other was of too high resistance to measure with the simple apparatus used, as were all samples with less than 40% Te.

### 3. Photovoltage

If a junction is formed between a conductor and semiconductor, the energy bands of the semiconductor will, in general, be bent because of charge transfer between the two materials. If this region is now illuminated, the charge carriers produced are separated by the field, giving rise to a photovoltage which can



be measured in an external circuit. The photovoltage on an EC-Se junction was about +0.2 v., while that on EC-40% SeTe junctions was about +0.1 v. A possible energy band picture is shown in Fig. 8.

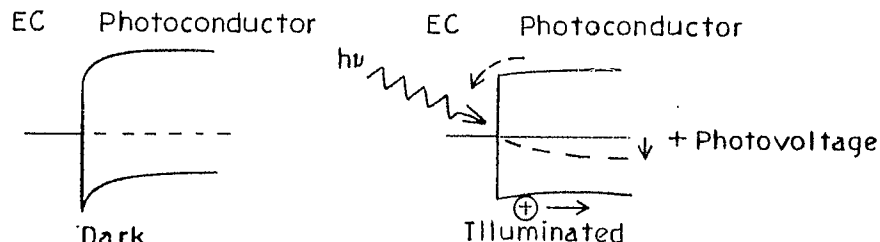


FIGURE 8. Possible Energy Bands at Plate-Substrate Junction

This sample model may be complicated by the Dember effect,<sup>7</sup> in which the more mobile charge carrier diffuses away from the illuminated region, setting up a potential difference. The two effects have not yet been separated.

#### 4. Dark Currents

Dark current was measured as a function of applied field on plates with various thicknesses of 40% SeTe between EC substrate and selenium. These are shown in Fig. 9 and 10. With positive polarity on the selenium surface, the structures behave approximately as though all contacts are noninjecting, with the pure selenium film most closely approaching ohmic characteristics (in which  $i \propto v$ ). With the selenium negative, however, dark currents on two of the structures show a tendency to rise at a power significantly greater than one for applied fields of above two volts/micron. There is also a dependence on SeTe thickness. This suggests that the SeTe layers act as injecting contacts for holes, and that space-charge-limited currents are being obtained. The selenium film again exhibited ohmic behavior.

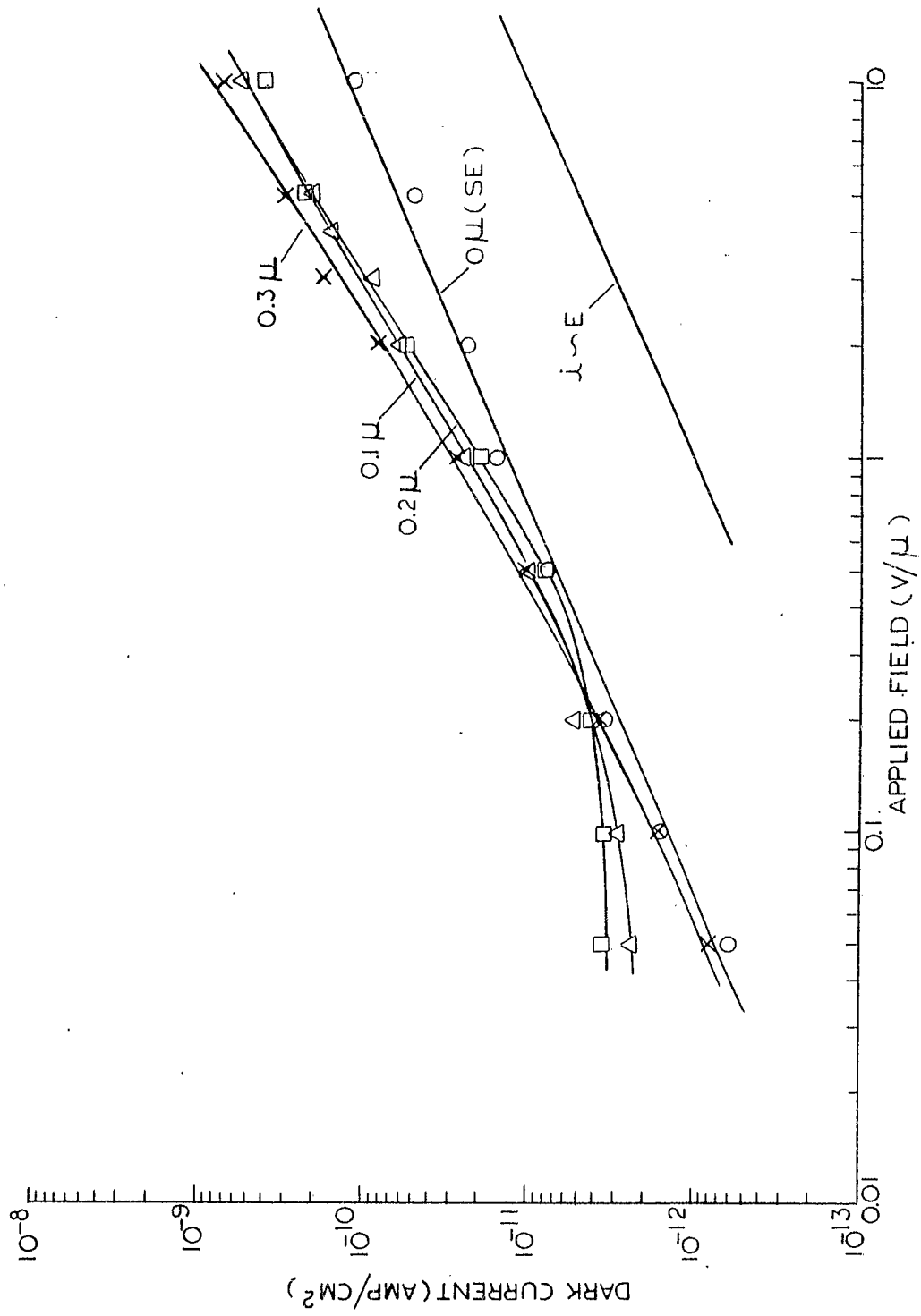


FIGURE 9. Dark Current vs. Field. Plate 970-45: EC + 40% SeTe + 20 μ Se. Positive

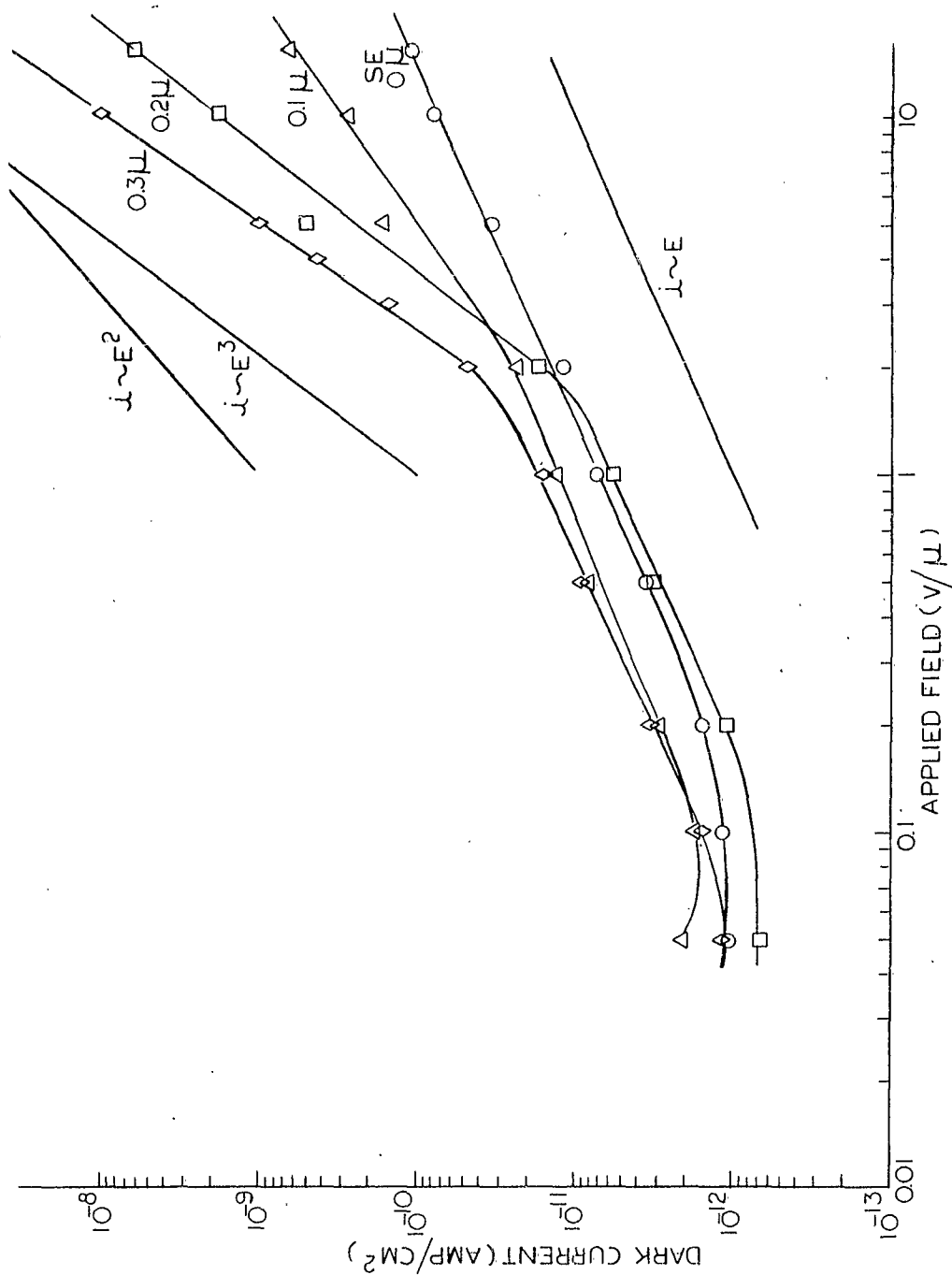


FIGURE 10. Dark Current vs. Field. Plate 970-45: EC + 40% SeTe + 20 μ Se. Negative

XEROX

#### IV. METHODS RESEARCH

##### A. FROST DEVELOPMENT

###### 1. Introduction

The image-forming member of the photographic system under discussion is a plastic layer coated on a flexible, conductive, transparent substrate. A charge pattern is transferred to the plastic layer from the photoconductor. Upon heating, the plastic layer becomes frosted (rippled) in an amount related to the magnitude of the density of the transferred charge. The resulting image can be viewed in an optical system designed to discriminate between the light scattered by the frost pattern and the light transmitted without deviation.

This section deals with studies of frost development, its sensitometric properties and processing requirements. Materials are identified according to the nomenclature of the previous interim report.<sup>(1)</sup> This report should also be consulted for a description of some of the experimental apparatus.

###### 2. Frost Sensitometry

A series of experiments was performed in which Resin Compound X-2 films, corona-charged,\* were heated at various temperatures for 25 seconds. Copper-coated microscope slides, used as substrates, were dip-coated and then baked at 50 degrees centigrade for one hour. The resin film thicknesses were measured with an interference microscope; frost cell sizes were determined by 1) photographing the frost at a position corresponding to an optical density of 0.5, 2) counting the number of intersections of the cell walls with a straight line drawn on the photograph, and 3) dividing the distance subtended by the line on the frost sample by the number of intersections. Samples were heated on a platen, using a film of silicone oil to improve the thermal contact, in order to bring about frost development.

Some results of these experiments are shown in Fig. 11, where optical density is plotted as a function of initial film potential. Film thickness was approximately  $3.7 \mu$ . Perhaps the most striking feature of these curves is that the potential required to obtain a given frost density decreases with increased heating. Increasing temperature results primarily in a shift of the characteristic curves along the potential axis toward lower voltages. To a lesser extent the characteristic curve slope decreases and the cell size increases with increased heating. The

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\* See first interim report<sup>5</sup> for description of wedge-charging apparatus.

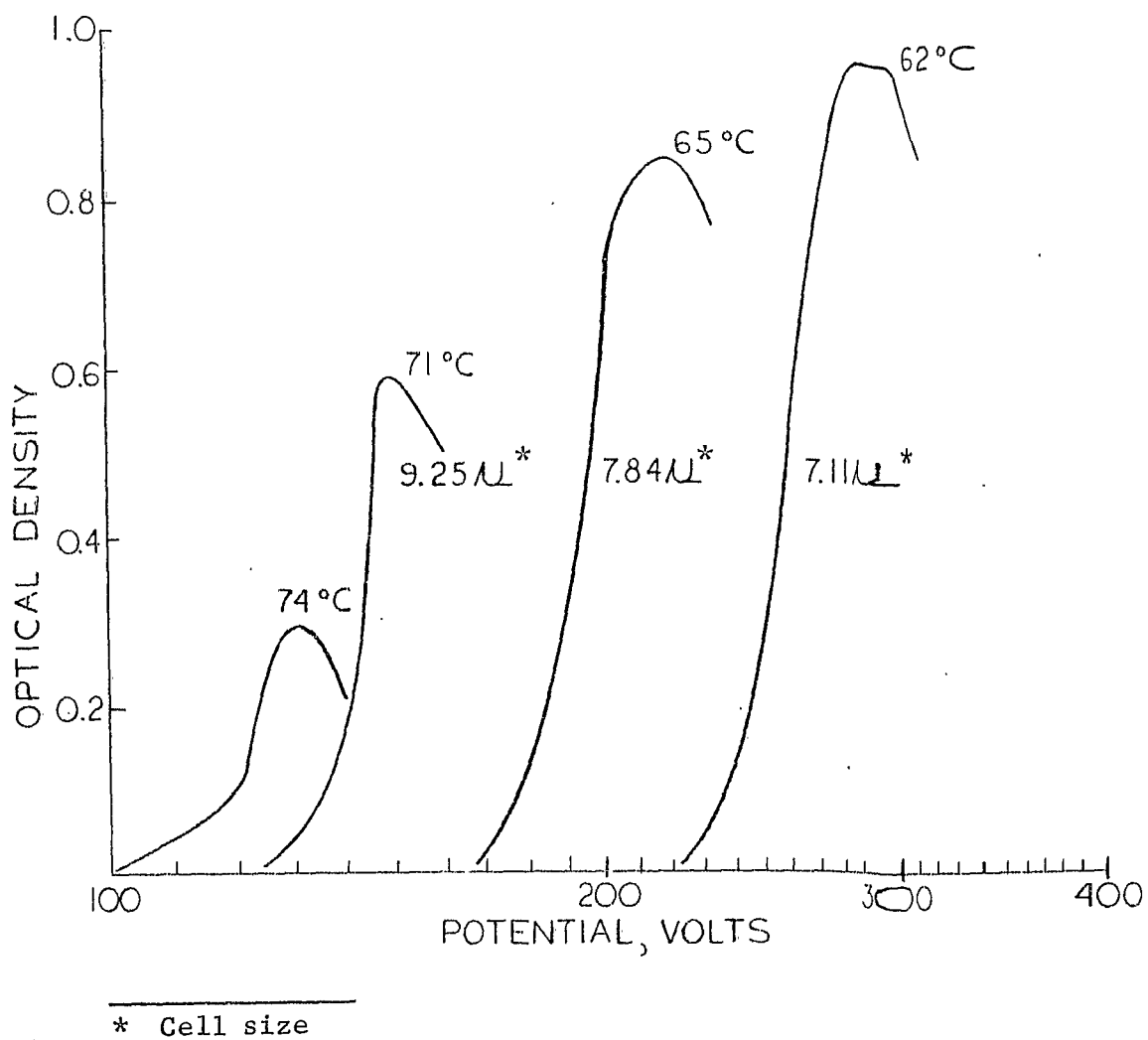


FIGURE 11. Optical Density as a Function of Potential for Resin Compound X-2 Films Developed Dry

maximum frost density increases with increasing film potential. Higher potentials than those shown in Figure 11 were attempted, but charging at higher currents causes the films to break down resulting in circular areas that are not frosted.

It would be extremely worthwhile if the heating conditions leading to proper frost development could be specified in general terms. As an initial attempt at such a specification, it might be theorized that, under conditions leading to a given frost density, the quantity

$$\frac{\eta}{tp} = \text{constant} \quad (1)$$

where  $\eta$  is the viscosity,  $t$  is the heating time, and  $p$  is the electrostatic pressure that tends to cause deformation. Regarding the deformable plastic layer as a parallel-plate capacitor would allow one to calculate the normal pressure on the film due to electrostatic charge. However, it is believed that this pressure is not that which produces frost, and it seems somewhat more proper to substitute an expression proportional to the electrostatic energy for  $p$ , as has been done by Dr. Cressman.<sup>4</sup> Equation (1) then becomes

$$\frac{\eta d}{tV^2} = \text{constant} \quad (2)$$

where  $d$  is the deformable plastic thickness and  $V$  is the potential required to obtain a given frost density. To test the frost data for constancy of the "frost function" of Eq. (2), it is necessary to know the viscosity of Resin Compound X-2 over a range of temperatures. In Xerox-supported work previous to this contract, it was shown that this viscosity -- measured by the falling-sphere method, over the temperature range 99.5 to 140 degrees centigrade -- follows the relationship

$$\log_{10} \eta \text{ (poises)} = 7.30671 \times 10^3 \frac{1}{T(^{\circ}\text{K})} - 17.01082 \quad (3)$$

Assuming that values extrapolated from this relationship are correct at the lower temperature of interest here allows one to calculate the "frost function." The results of such a calculation are summarized in Table I for the data of Fig. 11 and for additional data taken on films of other thicknesses.

TABLE I.

DATA FOR CALCULATION OF THE "FROST FUNCTION" FOR DRY FILMS

T	$\eta$ (poises)	$V_{D=.4}$ (volts)	$(V_{D=.4})^2$	d (microns)	$\frac{nd}{tV^2}^*$
62	$62 \times 10^3$	254	$6.44 \times 10^4$	3.9	0.150
65	$39.4 \times 10^3$	194	$3.76 \times 10^4$	3.7	0.150
70.9	$17 \times 10^3$	145	$2.10 \times 10^4$	3.7	0.120
61.6	$65.3 \times 10^3$	165	$2.72 \times 10^4$	1.76	0.169
65	$39.4 \times 10^3$	123	$1.52 \times 10^4$	1.85	0.192
68	$25.4 \times 10^3$	127	$1.61 \times 10^4$	2.38	0.150

\* poise micron sec<sup>-1</sup>volts<sup>-2</sup>

An optical density of 0.4 was arbitrarily chosen as the reference value. This necessitates eliminating data for the film heated at 74°C because the optical density was less than 0.4.

It is observed that the "frost function" does hold remarkably constant for these data. Over a temperature range<sup>2</sup> that causes an approximately fourfold change in viscosity,  $nd/tV^2$  varies from a minimum of 0.120 to a maximum of 0.192. This variation appears not to be correlated directly with the independent variables of this experiment.

### 3. Effect of Silicone Fluid on Heat Development

It was pointed out in the previous interim report<sup>5</sup> that silicone fluid left on the deformable plastic layer from the charge transfer operation has a substantial effect on the subsequent frost development. The main effect is a reduction in the threshold potential. Another effect previously cited, an increase in the maximum frost density, was believed to have been observed. However, it now appears that the maximum densities are similar for the two cases. Sufficiently high potentials were not previously employed to determine the "dry" development maximum density. As the following data clearly show, however, the optical density of film developed with an oil film is much higher for the same charge density.

Experiments similar to those of Fig. 11 and Table I were performed for silicone oil-coated films. In addition to two series in which the samples were heated at various temperatures for a constant time, a series was run in which temperature was held constant and heating time was varied. Just prior to the wedge-charging operation, a thin film of 50 cs\* silicone oil was applied to the Resin Compound X-2 film. At the shorter heating times (e.g., five seconds) it is possible that the actual heating times are significantly lower than the tabulated values because of the time required for heat conduction through the substrate. Densities were measured after removing the oil with a running water rinse.

The results of these experiments are given in Table II. These results are similar to those obtained with dry films, but the potentials are much lower. In Fig. 12 the optical density is plotted as a function of temperature for set B of Table II, the most consistent set obtained. Over the range of temperature from 68.5 to 62.0 degrees centigrade the maximum frost density remains fairly constant; increased temperature results primarily in a shift of the characteristic curve along the potential axis toward lower voltages.

The following differences are noted between "wet" and "dry" development:

1. Dry films require greater charge density to give the same optical density under equivalent conditions.
2. For dry films the maximum optical density that can be obtained under a given set of conditions decreases as heating temperature (and, presumably, time) is increased, whereas the maximum optical density is fairly constant over a temperature range with oil-coated films.
3. At 25-second heating times (and presumably other periods), oil-coated films can be heated at a higher temperature without loss in optical density -- this results in greater charge sensitivity. For example, silicone oil-coated films heated 25 seconds at 79°C suffer approximately the same loss of maximum density (because of overheating) as do dry films heated the same length of time at 74°C. The ratio of the viscosity of Resin Compound X-2 at 74°C to that at 79°C is approximately 2.

The data of Table II can be used to test the concept of the "frost function,"  $\frac{\eta d}{tv^2}$ , for "wet" development. Calculated

values are given in Table III.

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\* cs = centistoke



TABLE II.

PROPERTIES OF FROST-DEVELOPED RESIN COMPOUND X-2  
FOR VARIOUS TIMES AND AT VARIOUS TEMPERATURES

Set	Film Thickness ( $\mu$ )	Development		Cell Size ( $\mu$ )	Maximum Density	Potential for	
		Time (sec)	Temp. (°C)			D <sub>0.4</sub> (volt)	D <sub>0.5</sub>
A	2.46	25	63	--	0.1	--	--
	2.11	25	66.2	3.71	0.9	79	68.5
	2.29	25	69.1	5.01	0.96	73	62
	1.45	25	72.0	4.03	0.8	43	39.5
	1.59	25	75.0	3.92	0.7	40.5	36
	1.41	25	78.0	4.85	0.48	41.5	36.5
	1.76	25	84.0	--	0.11	--	38
B	1.2	25	62.0	2.08	0.59	89	64
	1.2	25	64.0	--	0.69	69.5	50
	1.2	25	66.0	--	0.66	62.5	49
	1.2	25	68.5	2.5	0.68	50	41.5
	1.2	25	72.0	--	0.56	43	36.5
	1.2	25	75.0	3.12	0.51	39	34.5
	1.2	25	79.5	--	0.22	--	30
	1.2	25	81.0	--	0.0	--	--
C	--	5	72.0 ( $\pm 0.5$ )	--	0.00	--	--
	1.59	10	72.0 ( $\pm 0.5$ )	3.36	0.78	56	45
	1.59	20	72.0 ( $\pm 0.5$ )	3.41	0.76	46.5	40
	1.59	30	72.0 ( $\pm 0.5$ )	3.55	0.72	37	32
	1.94	45	72.0 ( $\pm 0.5$ )	5.45	0.92	42	35
	1.76	56	72.0 ( $\pm 0.5$ )	4.65	0.70	38	34
	1.68	75	72.0 ( $\pm 0.5$ )	5.76	0.70	49.5	45
	1.94	120	72.0 ( $\pm 0.5$ )	6.61	0.42	45	40

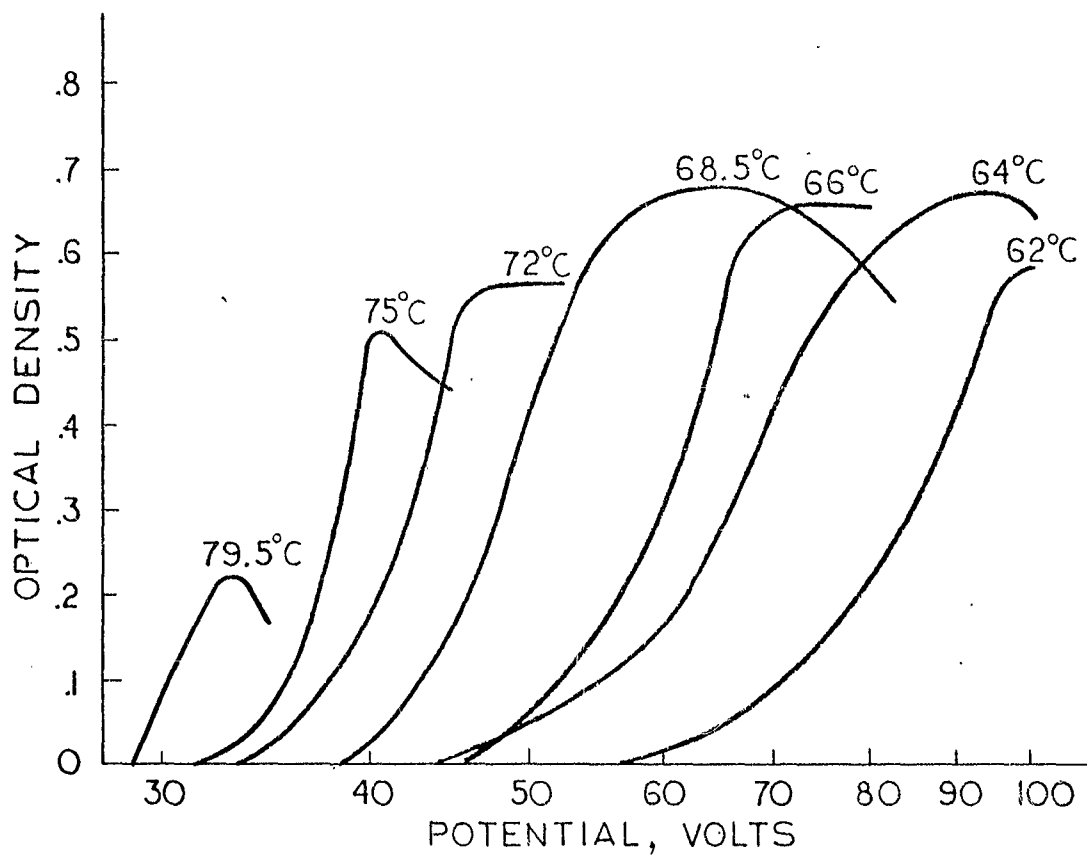


FIGURE 12.. Optical Density of Frost as a Function of Potential for Films Developed While Covered with Silicone Fluid

TABLE III.

TEST OF "FROST FUNCTION" FOR DATA OF TABLE II

Set A			Set B			Set C		
Time (sec)	Temp. (°C)	$\frac{\eta d^*}{t V^{0.4}}$	Time (sec)	Temp (°C)	$\frac{\eta d}{t V^{0.4}}$	Time (°C)	Temp (°C)	$\frac{\eta d}{t V^{0.4}}$
25	66.2	0.452	25	62.0	0.377	10	72	0.736
25	69.1	0.378	25	64.0	0.455	20	72	0.534
25	72.0	0.455	25	66.0	0.419	30	72	0.561
25	75.0	0.372	25	68.5	0.455	45	72	0.356
25	78.0	0.210	25	72.0	0.376	56	72	0.316
			25	75.0	0.305	75	72	0.133
						120	72	0.116

\*Poise micron sec<sup>-1</sup> volts<sup>-2</sup>

The "frost function,"  $\eta d/tV^{0.4}$ , does hold relatively constant for the data of sets A and B. Excluding the values for the highest temperature in each set, because the frost densities are low for this temperature, the function varies from a minimum of 0.372 to a maximum of 0.455. In the range 62 to 75 degrees centigrade the viscosity of Resin Compound X-2 varies by a factor of over six. In the case of the constant temperature data of Set C, the "frost function" diminishes as time is increased, and one is tempted to conclude that  $\sqrt{t}$  should be substituted for  $t$  in Eq. (2). However, more theoretical work and experiments over a wider range of the variables are required before further conclusions can be drawn.

The reason for the increase in frost sensitivity caused by a film of silicone fluid on the resin layer during development has not yet been definitely established, but this behavior is consistent with the frost theory of Dr. Cressman.<sup>4</sup> In this theory the self-repulsive forces of the surface charges oppose surface tension forces. Frosting occurs when the electrical force exceeds the surface tension force. Because silicone fluid reduces the interfacial tension of the resin layer, it should reduce the charge density required for frost.

It has been found that thinner films can be frost-developed if oil is used. The minimum frostable thicknesses of dry and oil-coated Resin Compound X-2 films are, respectively, approximately 0.8 and 0.4 micron. The 0.4-micron, oil-coated films have a maximum optical density of 0.15 (f/4 reflection system), and a grain size of 1.4 microns. Evidently the 0.4-micron films can not maintain sufficiently high charge density to frost when dry, but can maintain the lower charge density required to frost when oil-coated.

#### 4. Simultaneous Measurements of Frost Density and Film Potential

The complicated dependence of frost density on film thickness, film potential, film heating temperature (or viscosity) and film heating time is not yet completely understood either from an empirical viewpoint or from a fundamental viewpoint. Such knowledge could help greatly in comparing materials and in determining optimum operating conditions. For these reasons new equipment was assembled that simultaneously records the optical density and the electrostatic potential of frost films during the heating cycle. Measurements with this device should provide a more accurate and rapid means for determining:

1. Maximum frost density as a function of thickness, material, age, or other important variables.
2. Optimum heating time as a function of temperature.
3. Effects of liquid films on frostable layers during development.
4. Threshold potentials.

In addition, the information gained with this device should aid in testing theories of frost development mechanisms. Measurements with the equipment so far have been helpful in clarifying the nature of the threshold potential.

Figure 13 shows typical data obtained by simultaneous measurement of voltage and optical density. In these measurements one-micron Resin Compound X-2 films were coated on brass substrates and placed on a hot plate maintained at 60°C at time = 0. There is a small, rapid initial drop in potential that is evidently associated with heating the film. The films then begin to frost -- films charged to higher potentials frost more rapidly. There is an abrupt decrease in potential concurrent with frosting. Peak density is reached only after the coating is discharged to 50 per cent, or less, of its initial value. After this, density falls rapidly at first and then more slowly.

Measurements were made on 3.8-micron, 1.8-micron and 1.0-micron films at a range of initial potentials. A plot of maximum frost density versus film potential (Figure 14) indicates a definite potential limit below which no frosting occurs. This limit appears to be a true threshold potential. This threshold differs from the threshold previously described in early work on this project in that it can be described rather precisely. In earlier work the film potential - frost density characteristic curve was not known to vary widely, depending upon heat development conditions, and the threshold was taken merely as the potential at the toe of "the characteristic curve." It is now clear that there is no unique characteristic curve and it is necessary to define the threshold as the highest potential below which frost will never occur regardless of heat development conditions. When the maximum densities of the frost characteristic curve data for 3.7-micron films reported above are plotted against the film potential (Figure 15) a threshold potential is indicated that is in acceptable agreement with that obtained from Fig. 14 for 3.8-micron films.

Two points should be mentioned in connection with Fig. 13 and 14. In Fig. 14, the so-called "initial potential" is the potential measured 0.25 minute after the sample was placed on the hot plate. This type of potential gave a more consistent correlation with other variables than did the true initial reading. Secondly, it should be noted that the frost optical density readings in all previous reports were measured on the moving-table densitometer device, whereas a different device is used for the simultaneous density-potential measurements. These devices are in rough agreement at densities below 0.7, but diverge for higher densities; a reading of 0.9 on the moving-table device was obtained with a film which measured 1.24 on the simultaneous device.

Simultaneous measurements are in progress at higher temperatures. Under such conditions development times less than one second can be readily achieved.

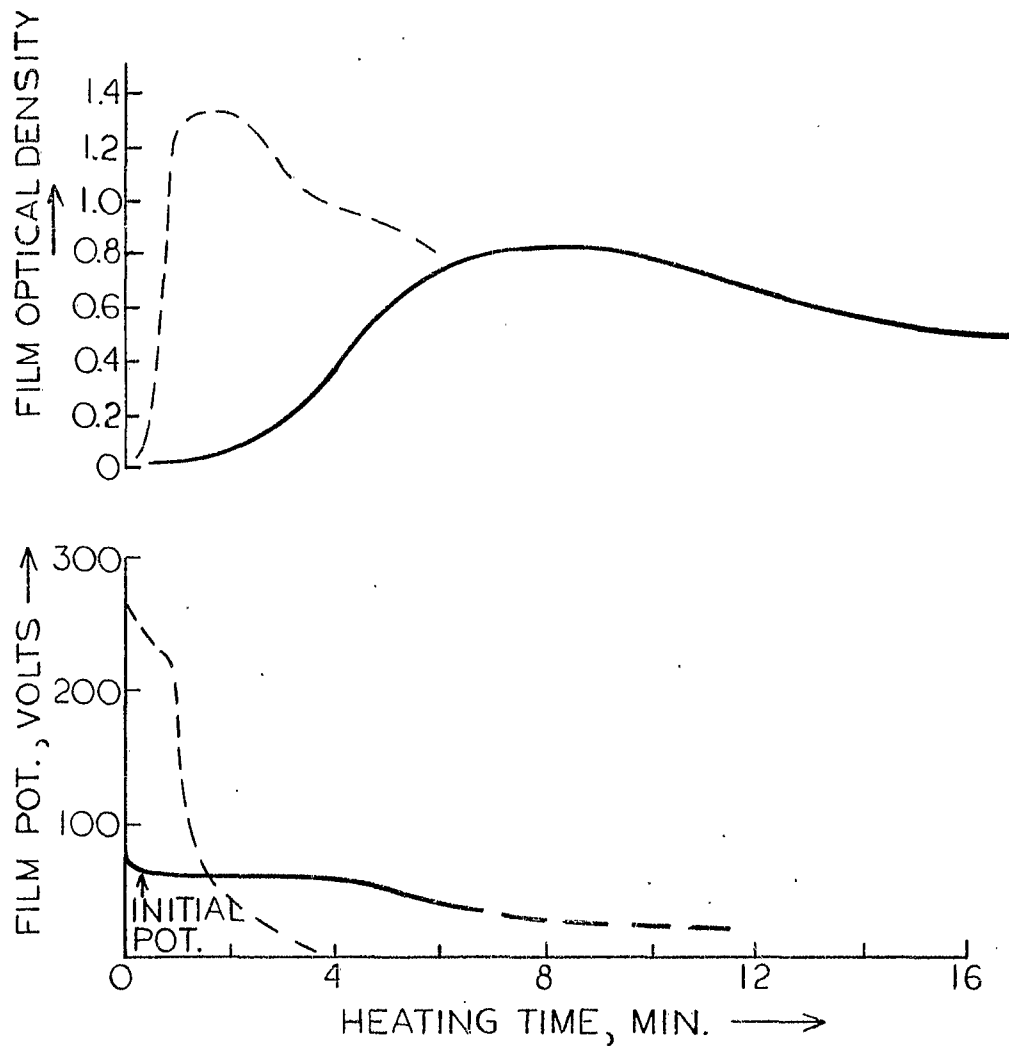


FIGURE 13. Typical Density-Voltage Measurements for a Film Charged to a High Potential (dashed curve) and to a Low Potential (solid curve). Data are for  $1\ \mu$  Resin Compound X-2 Films Heated at  $60^\circ\text{C}$ .

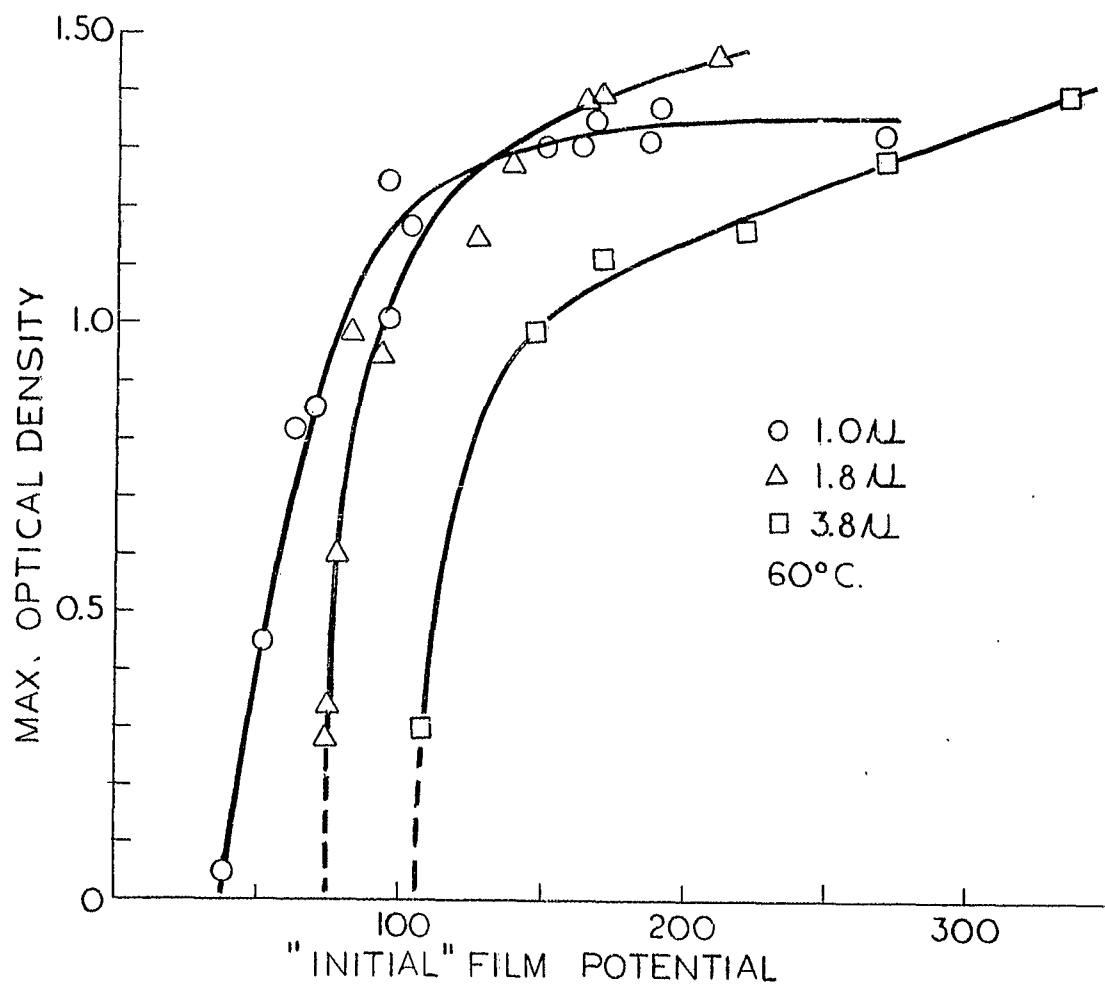


FIGURE 14. Maximum Optical Density as a Function of Potential  
 0.25 Minute after Sample was Placed on Hot Plate

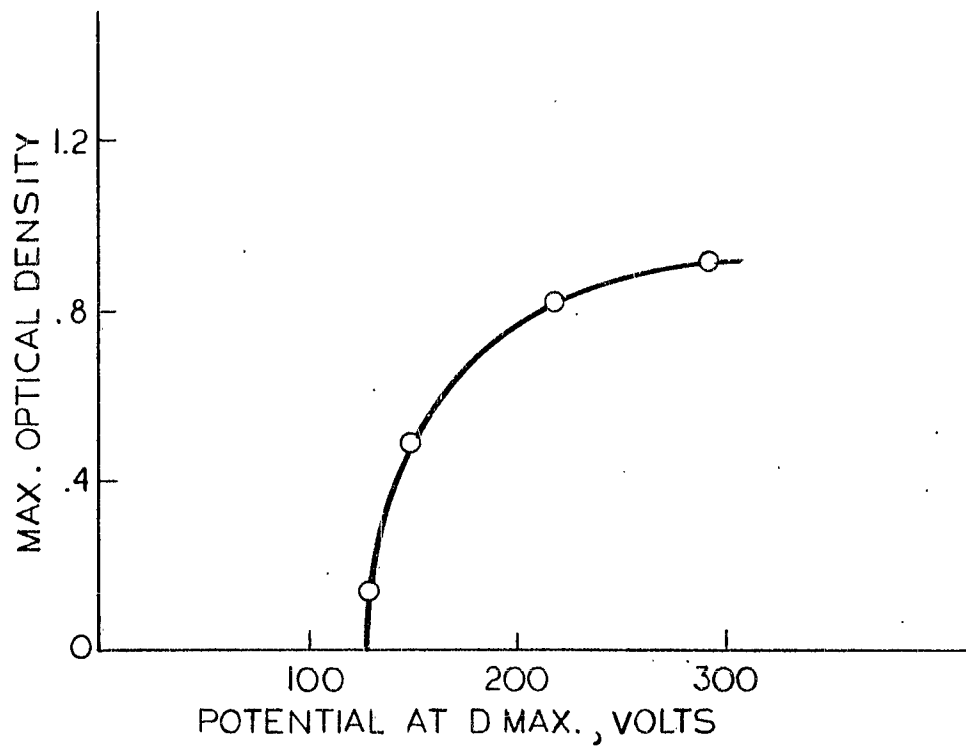


FIGURE 15. Maximum Optical Density of 3.7  $\mu$  Resin Compound X-2 Films as a Function of Potential at the Maximum Density (from data of Fig. 11)



## 5. Frost and Relief Imaging Contrasted

In some of the discussion to follow reference will be made to relief images. Because both frost and relief may be present in the same image, it is worthwhile to review<sup>3</sup> the meaning of these terms. Frost is a random, minute dimpling observed when the charge density is uniform or smoothly varying. Relief deformation consists of a continuous narrow depression and adjoining ridge developed at a charge boundary, i.e., where the charge density changes abruptly, such as at electrostatic image edges. Although both types of deformation can be observed in the same film, relief deformation, if it occurs, will occur sooner in the heating step and to some extent can inhibit or prevent frost deformation immediately next to the relief edge.

### B. CHARGE TRANSFER

#### 1. Introduction

In the photographic system under discussion a thin layer of liquid is inserted between the free surface of the photoconductor and the deformable plastic layer. The purpose of this liquid is to transport the charge released by light in the photoconductor to the plastic film. As was explained in the previous interim report,<sup>5</sup> it was at first believed, as a result of work at Xerox prior to the present contract<sup>2</sup>, that highly insulating liquids could perform this function. At this time it was assumed that the mechanism of charge transfer was akin to a breakdown effect with a very low threshold potential (less than 10 volts, perhaps), because it was known that the liquids used (principally Dow Corning 200 Silicone Fluid, 50 cs) were excellent electrical insulators. Work on this project has since shown that the level of conductivity in pure silicone fluids is too low for this. The previous good results must be explained by contamination.

However, the fact that good results were obtained by the liquid charge-transfer technique is clear, and the obvious direction of research has been to study the use of well-characterized liquids with conductivities suitable for charge-transfer imaging. Despite the serious questions that must be raised regarding resolution losses in semiconducting liquids, the liquid system still possesses many attractive qualities when compared with charge transfer systems employing gas breakdown. These include:

1. Very low or no threshold potential.

2. Gap must be kept small but probably doesn't require control of minimum as well as maximum thickness
3. System doesn't require gas atmosphere

The present section deals with efforts to characterize liquids more precisely by "classical" measurements of electrical parameters and also covers practical studies of various liquids in the actual charge-transfer system.

## 2. Basic Studies

Understanding of the fundamental mechanism of liquid conductivity in the materials used for charge transfer would be extremely helpful in determining the theoretical optimum performance of the charge-transfer system and in guiding applied studies. As a beginning it was decided to measure the resistance of charge-transfer liquids under pulse conditions. Direct-current measurements had been made on a number of these liquids, but results were rather unsatisfactory because values drifted with time<sup>5</sup>. It appeared likely that the transient resistance of thin liquid films would be considerably lower than the d.c. values, and that relatively simple circuitry might suffice for the measurements. This viewpoint was suggested by some data in the literature such as that on hexane due to K.A. Macfadyen<sup>6</sup> that indicated an increase of conductivity by a factor of 500 under pulse conditions compared to d.c. values.

A block diagram of the final arrangement for measuring transient resistances is shown in Fig. 16. The two output pulses from the Schering bridge circuit (Fig. 17) ideally are identical except for the desired d.c. component due to the resistance of the sample. The pulses consist mainly of resistance-capacitance (RC) transients caused by applying the input pulse to the RC network. The output pulses were fed into a Tektronix Type Z Differential Preamplifier which has a rejection ratio of 40,000 to 1 at one kilocycle. The desired output from the Type Z preamplifier arises only from asymmetries of the two pulses from the bridge circuit (one from the sample and one from the standard capacitance). Small unwanted signals will come from base line disturbances and leakage through the tube and transistor capacitances of the preamplifier.

The pulse generator is capable of applying  $\pm 500$ -volt pulses across the oil samples. A pulse duration of 200 microseconds was used in the most successful experiments. The smallest detectable signal from the bridge circuit was between 0.5 and 1 millivolt. Several liquids with resistivities much lower than silicone oil were used to test the equipment and procedure. The following resistivities were obtained: ethyl alcohol,  $\rho = 5 \times 10^6$  ohm-cm; chloroform,  $\rho = 2.5 \times 10^7$  ohm-cm; and "3-in-1" oil,  $\rho = 2 \times 10^{10}$  ohm-cm.

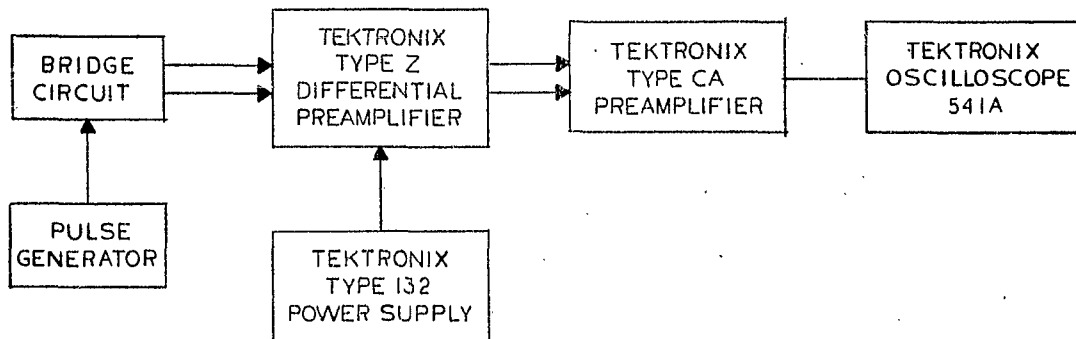


FIGURE 16. Block Diagram of Resistivity Bridge

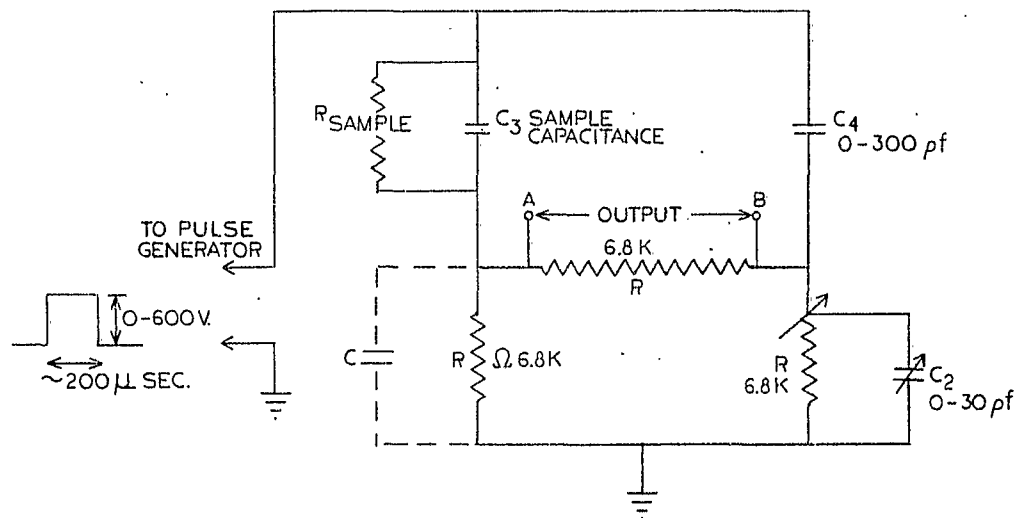


FIGURE 17. Schematic Diagram of Schering Bridge Circuit

A considerable amount of time was spent to improve and determine the ultimate resistivity-measuring capability of this arrangement. The highest measurable resistivity can be estimated as follows: the smallest signal which can be unambiguously measured is  $\approx 1$  millivolt across the 6,800-ohm resistance for an input pulse of 300 v. (this is one part in  $3 \times 10^5$  compared to the maximum rated discrimination of one in  $10^4$ ). This gives an electric field of  $\approx 3 \times 10^5$  volts/cm across a 12-micron-thick oil film, the smallest practical thickness. The resulting resistivity is  $\approx 1 \times 10^{12}$  ohm-cm.

Pulse measurements using Octoil\* gave values of  $1.7 \times 10^{12}$  ohm-cm. and later  $1.0 \times 10^{11}$  ohm-cm. The latter two values agree well with the result obtained from a General Radio Capacitance Bridge, namely  $1.3 \times 10^{11}$  ohm-cm. Consecutive measurements on Liquid 34B\*\* gave the following results:  $\rho = 5 \times 10^{11}$ ,  $1.4 \times 10^{12}$ ,  $3 \times 10^{12}$  and  $>3 \times 10^{12}$  ohm-cm. Severe difficulties hamper consistent results in this region: first this is the upper limit of measurement so that the signal-to-noise ratio is low; second, the high electric fields needed to obtain a measurable current cause breakdown through the oil sample especially if impurities are present, or imperfections exist in the electrodes (which were evaporated gold-coated microscope slides); third, there is evidence that the thickness of the oil film changed with time.

In view of these difficulties and the fact that the desired range of d.c. resistivities of interest is  $\sim 10^{12}$  to  $10^{15}$  ohm-cm., which is outside the range of this instrument, it was decided not to continue the pulse measurements.

### 3. Practical Measurements of Liquid Behavior

At present, the simplest tenable assumption concerning the charge transfer-resolution characteristics of liquid coupling agents is that conductivity in the liquid is ionic in nature. Although no attempt has been made to show this definitely, it has been observed that liquid conductivities tend to increase as viscosity is reduced. This would be expected if ions conduct the current, because ion mobility should be inversely proportional to viscosity. Unfortunately, very low viscosity polysiloxane liquids can not be used for the present application because of their solvent effect on Resin Compound X-2. It was therefore attempted to increase the conductivity of pure 50 cs silicone fluids by the use of chemical additives.

#### a. Doping Studies

As a beginning of this study, the charge-transfer characteristics of 23 silicone oil samples were measured. These samples of silicone oil were doped with water, organic and inorganic

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\* Octoil - Consolidated Vacuum Corp.

\*\* See Table VI (p. 42).

metal compounds, various imines, and similar materials to give a range of liquid conductivities. It was found that charge transfer varied through these samples from zero to the maximum obtained with Octoil. Undoped Octoil transferred 100% of the expected charge in one half of a second, the time used in these experiments.

Two of the organometal compounds found in these tests increased the conductivity of 50 cs polysiloxane (silicone oil) to values that were of interest as examples of relatively high (Liquid 34) and relatively low (Liquid 21) conductivity.

To characterize these liquids in somewhat greater detail than obtained from the initial screening, they were compared for charge transfer at various pulse durations. White light was used at constant intensity. The "short" duration (the period the substrates are electrically connected after pulsing but prior to separation) was 15 seconds. The potentials measured on the Resin Compound 6 electrodes are given in Table IV. The electrode material used for these tests is not a good frostable material but is useful for electrical tests of various liquids because it is relatively inert in comparison to Resin Compound X-2.

TABLE IV

COMPARISON OF CHARGE TRANSFER OF LIQUIDS 21 and 34

Pulse Duration (sec)	<u>Electrode Potential (volt)</u>	
	<u>Liquid 21</u>	<u>Liquid 34</u>
1/2	56	98
1/5	26	50
1/10	14	26
1/25	2	8

These results show that, in the range studied, the electrode potential is approximately proportional to the pulse duration and that, with 15-second "short" durations, Liquid 21 transfers approximately one half of the charge of Liquid 34. With five-second "short" durations and one-half-second pulses, this ratio is approximately one-to-five. Under the latter

conditions the quantum efficiency using a conventional selenium plate is approximately 33 per cent with Liquid 34.

#### b. Liquid Layer Thickness

When a relatively low conductivity liquid is used for charge-transfer under conditions leading to less than complete transfer of the charge, differences in charge transfer due to liquid layer thickness variations can be demonstrated. Methods of measuring the liquid layer thicknesses have been difficult to devise, and this has hindered a precise determination of the effects of variations. Interference-microscope methods have been attempted, but even with especially metallized polyester films, results have been poor. One simple technique has been devised, however, to allow determination of average liquid film thicknesses. In this method a small, known volume of silicone oil is inserted between a rigid flat member (simulating the photoconductor) and a thin polyester film. Average thickness is calculated from the area. Using this technique, presently used film thicknesses were found to be approximately 0.8 micron. The present method of contacting the film to the photoconductor utilizes a small diameter (~1/4 inch) Tygon-covered metal roller to roll the plastic film onto the photoconductor simultaneously expressing the excess liquid. Using larger, softer rollers results in liquid layers approximately twice this thick.

#### c. Effect of the Contact Period

In work prior to the present contract it was found that electrically connecting the photoconductor and electrode substrates subsequent to the light exposure/potential pulse and during separation decreased the electrode potentials in the non-exposed areas but had little effect in the exposed areas<sup>2</sup>. By analyzing the potentials, after pulsing, on the electrode and on the photoconductor it appeared that charge was separated in the liquid by the applied field and accumulated on the electrode and photoconductor. The "shorting" operation allows these charges to recombine. When liquids of relatively low conductivity are utilized, the shorting period also provides additional time for charge released by exposure to migrate to the electrode. The fact that the field is no longer applied makes this collection period less efficient than that during pulsing, but the period is of some practical importance. Consider the following example: The charge transferred to an electrode, using Liquid 21, is approximately 1/3 that transferred using Octoil, for pulse times on the order of one second and for periods during which the substrates of the electrode and the photoconductor are connected approximately five seconds prior to the removal of the electrode. Thus for relatively short periods,

approximately one third as much charge is transferred by Liquid 21 as by Octoil.

If the electrode is left in contact with the photoconductor for longer periods it is found that larger amounts of charge transfer to the electrode up to a maximum value near that obtained with Octoil. This is shown by the data of Table V.

TABLE V.

ELECTRODE POTENTIAL AFTER TWO-SECOND PULSES  
FOR VARIOUS CONTACT TIMES

<u>Contact Time</u> (sec.)	<u>V<sub>electrode</sub></u> (volt)
5	-16
15	-26
60	-42
60	-48
15	-38
5	-22

It is thus clear that much of the charge released by exposure can be recovered at the electrode provided sufficient time is available and provided that photoconductor dark current during the contacting period can be neglected. However, some of the charge is lost, as can be seen from the following experiment.

Utilizing one-minute contacting periods and Liquid 21, the electrode potentials obtained with various light intensities and pulse durations were determined. Figure 18 shows that electrode potential is approximately proportional to exposure ( $I \times t$ ). However, there is a tendency for the lowest intensities to give the highest quantum efficiencies. This indicates that accumulation of charge at the photoconductor surface in short, high-intensity exposures decreases the charge yield at the electrode even with long contacting periods.

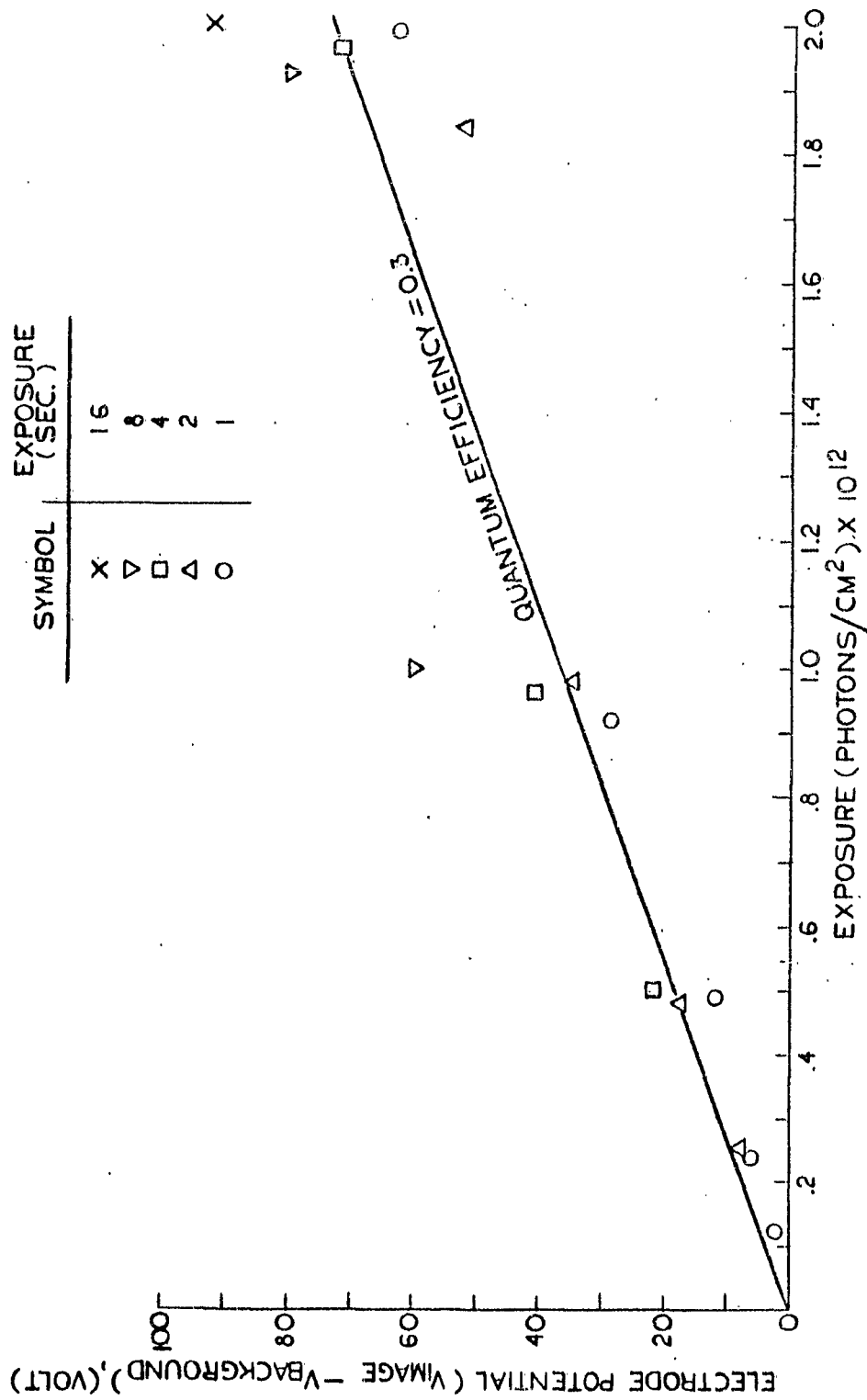


FIGURE 18. Charge Transfer vs. Exposure at Various Light Intensities.



#### d. Effect of Doping

Measurements were made of the quantity of charge transferred using concentrations of Organometal 2 in silicone oil ranging from 0.02 to 0.4 per cent with various plastics, exposure light intensities, and exposure times. The results of these experiments are tabulated in Table VI. In this work monochromatic illumination at 4000 Å was used for low-intensity measurements. To obtain higher light intensities it was necessary to employ white light; the relative intensities of the white light are indicated by the aperture of the light source. Charge was collected on electrodes coated with Resin Compound 6, approximately two microns thick. The "short-out" periods during which the electrode and photoconductor substrates were connected (following pulsing and prior to separation) were approximately five seconds in each case.

The data of Table VI are somewhat erratic, but some useful information can be abstracted. Taking the averages of the electrode potentials at various dopant concentrations and light intensities for 0.5-second pulses leads to the data plotted in Fig. 19. It is seen that, neglecting several wild points, electrode potential increases with dopant concentration and approaches a constant value, depending upon light intensity. It is interesting that the electrode potentials for low dopant concentrations are low, so that the curves do not pass through the origin or through the potential axis. This tendency for the low electrode potentials to be lower than expected is also illustrated in Fig. 20 in which electrode potential is plotted as a function of pulse duration. The potentials of the curves corresponding to the highest light levels, in Fig. 20, appear to pass through a maximum. This difficulty in collecting charges equivalent to potentials higher than approximately 75 volts has been observed repeatedly.

#### 4. Resolution as a Function of Liquid Conductivity and Processing Time

Tests were carried out to determine the manner in which the resolution of the charge-transfer process changes with processing time and liquid conductivity. High contrast parallel-bar resolution charts were projected by means of the special camera described in the previous interim report.<sup>5</sup> Using a Gurley (USAF 1951) resolution test chart, 300 line pairs/mm. can be resolved on Kodak High Resolution Plates under optimum conditions with this camera.

For resolution studies, charges were transferred from a conventional 20  $\mu$  selenium plate to Resin Compound X-2 electrodes. Several difficulties were encountered in making meaningful comparisons between various charge transfer liquids because the

TABLE VI.  
RESULTS OF CHARGE TRANSFER EXPERIMENTS WITH LIQUIDS OF DIFFERING DOPANT CONCENTRATION

# XEROX

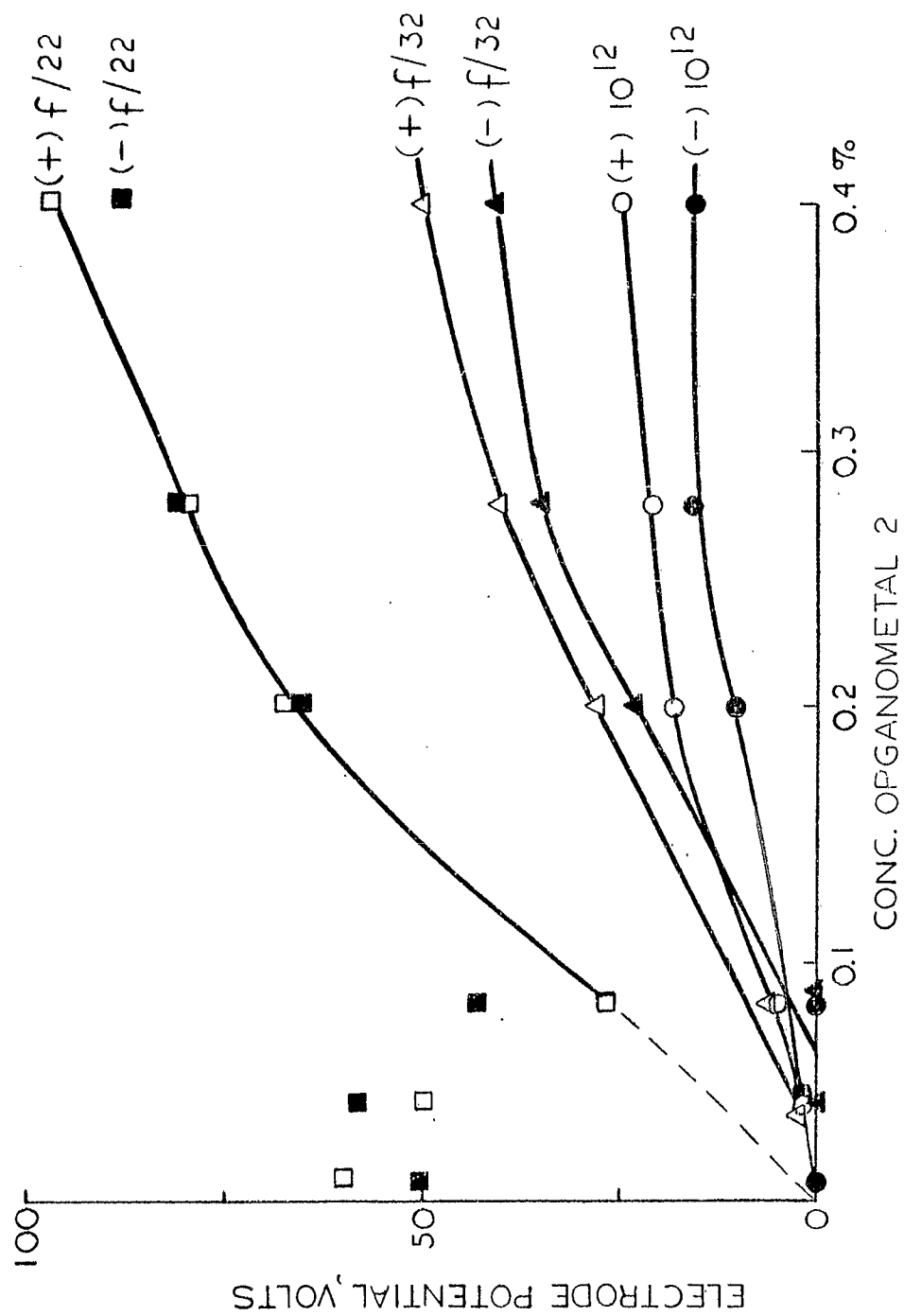


FIGURE 19. Average Electrode Potential as a Function of Dopant Concentration at Various Light Levels

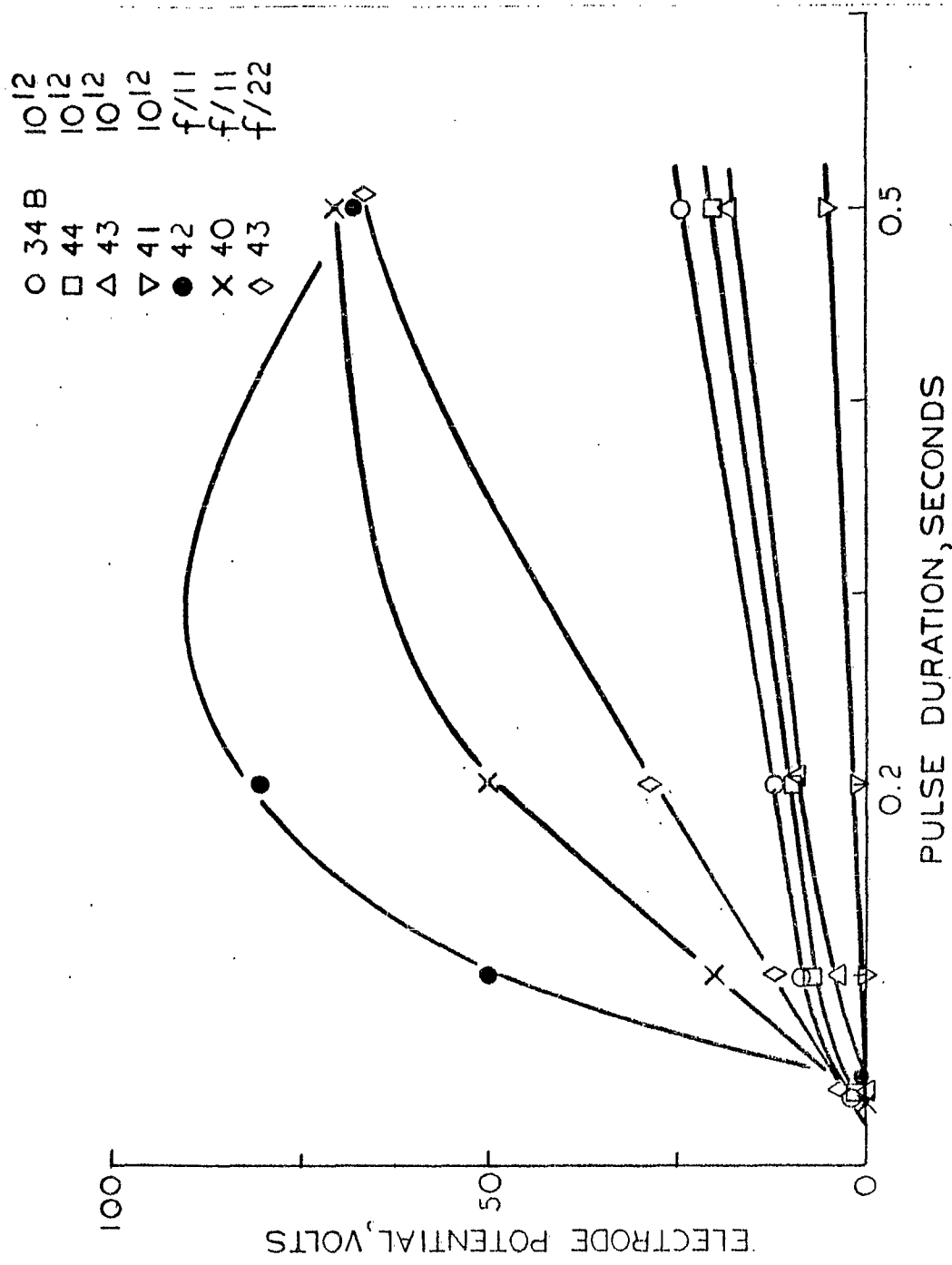


FIGURE 20. Electrode Potentials as a Function of Pulse Duration for Positive Electrode Polarities

completeness of charge transfer depends upon liquid conductivity. This was regulated somewhat by utilizing a longer shorting period for low-conductivity liquids. For example, the "short-out" period for Liquid 21 was two minutes, and for Liquid 34, five seconds. Heat development times were 15 seconds and 120 seconds for images transferred with Liquids 34 and 21, respectively. Other conditions were: exposure, approximately  $7 \times 10^{12}$  photons per square centimeter; heat development temperature, 67 degrees centigrade. Total processing time was varied by delaying the start of heat development after separation from the photoconductor for various lengths of time. This time period is referred to as "total time." In Fig. 21 resolution is plotted as a function of total time on a log-log plot. The graphs for different charge-transfer liquids are nearly parallel with a slope of approximately  $-1/2$ . This indicates a functional relationship given by

$$(\text{Resolution}) (\text{time})^{1/2} = (\text{constant})$$

It is seen that resolution is much lower with Liquid 34 and that it falls rapidly in the first minute, whereas the fall of resolution for Liquid 21 is less than the experimental error in the same time. Liquids 41 and 43, of intermediate conductivity, give intermediate results. See Tables IV and VI for comparison of these liquids (Note: the suffix A, B, etc. refers to the batch number when more than one was made.) Both frost and relief resolutions are given for the less conductive Liquids 21 and 41. Relief was not observed with the more conductive Liquids 34 and 43, presumably because charge gradients were too low.

More recent experiments indicate that the differences noted between frost and relief resolutions in the above experiment were due in part to the rather low charge densities used. Using higher charge densities and Liquid 43, a frost resolution of 41 lp/mm. was obtained.

#### 5. Fluorocarbon Liquids for Charge Transfer

It has been found that fluorocarbon fluids can be utilized as charge-transfer media. These materials can be doped to give higher conductivity than undoped liquids and, because of their rapid evaporation rate and chemical inertness, possess unique advantages for the present application. Tests consisted of measurements of the charge transferred to electrodes coated with two microns of Resin Compound X-2 from a selenium plate at various light levels. In addition to the pure liquids, doped liquids were also tested. For purposes of comparison, Liquid 34B was tested under the same conditions. These data are summarized in Table VII.

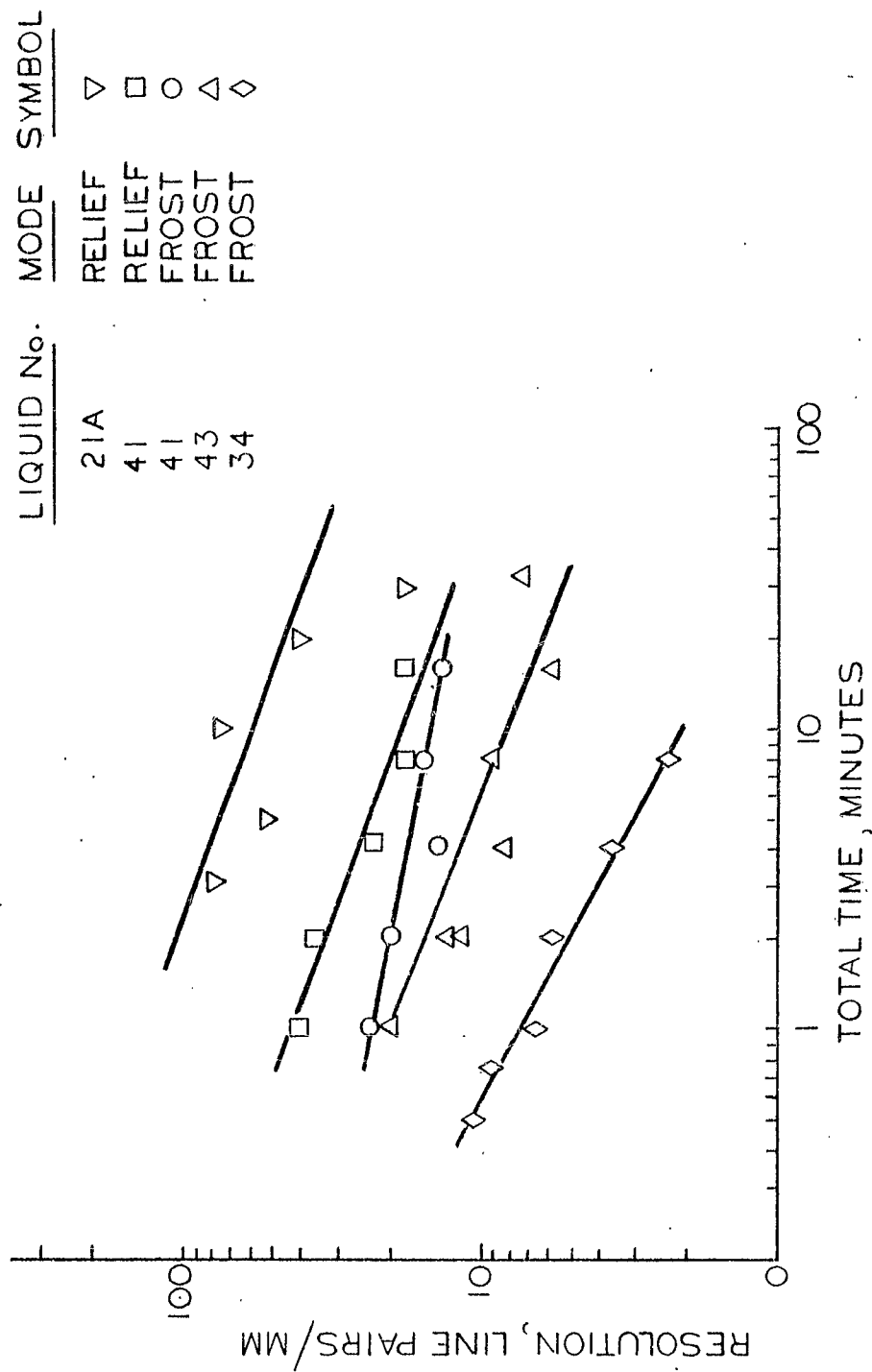


FIGURE 21. Resolution as a Function of Time for Various Charge-Transfer Liquids

TABLE VII.  
TESTS OF FLUOROCARBON LIQUIDS

Liquid Number:	34B	45	46	47	48	49	50
Composition:	silicone + Organometal 2	Fluoro- carbon 1	doped Fluoro- carbon 1	Fluoro- carbon 2	doped Fluoro- carbon 2	Fluoro- carbon 3	doped Fluoro- carbon 3
Applied Electrode Polarity:	-	+	-	+	-	+	-
Exposure Intensity*							
0.25 x 10 <sup>12</sup>	-10		-8	-5	-10	-9	-18
0.5 x 10 <sup>12</sup>	28 -26	0	0 -16	0 -28	0 -19	0 -16	4 -36
1.0 x 10 <sup>12</sup>	38 -43						
2.4 x 10 <sup>12</sup>	40 -50						
		-26	-50	-50	-146	-46	-96

\*At 4000 Å, 1 sec. pulse (photons/sq.cm.)

It will be noted that, in contrast to Liquid 34B, the fluorocarbon liquids appear to be more conductive for one polarity than for the other. The data in Table VII taken at  $2.4 \times 10^{12}$  photons/cm<sup>2</sup> are inconsistent because the exposure level is above the linear region for many of the liquids. (See Fig. 20.)

Liquid 49 was used to produce an image with 65 lp/mm resolution. This image was developed after the fluorocarbon charge-transfer liquid had evaporated. Because the image was produced with one exposure (no precharge), and because a high charge density was required to develop dry, the efficiency was low; an exposure of  $2 \times 10^{13}$  photons/cm<sup>2</sup> at 4000 Å was used. However, precharging should improve image quality further and should reduce the required exposure.

### C. SYSTEM STUDY

#### 1. Heat Development Methods

##### a. Platen Heating

Most of the experience in heat development of frost up to the present has been in heating by conduction from a heated platen. Mainly for convenience in developing by inspection, temperatures have been adjusted for development times of approximately one minute. However, brief experiments have shown that development times of approximately two seconds can be obtained with no loss in optical density by heating Mylar-supported films on a platen. Using heat-treated and silicone oil-coated Resin Compound X-2, the temperatures required to obtain 30-second and 2-second development times are approximately 66 degrees and 82 degrees centigrade, respectively. Development times less than two seconds can be achieved; two seconds is merely the shortest period possible with the manual development procedure if the images are to be removed from the platen at the optimum instant. Recent studies in which the optical density is recorded during heat development show that at temperatures of 100°C development to high density occurs in a fraction of one second.

Previously, most platen development work has utilized a silicon fluid layer to provide thermal contact between the platen and the film substrate. However, recent studies have shown that polyester-supported films can be developed equally well on a dry cylindrically shaped platen, provided enough tension is applied to the film to hold it uniformly against the platen.



#### b. Infrared Heating

Infrared (or radiant) heating has the advantages that heating units are commercially available, that warm-up times can be relatively short, that full-frame heating should be possible so that mechanical drives are not required, and that the resistance of the conductive substrate of the film need not be accurately controlled (as for resistance heating of the conductive layer).

One disadvantage of infrared heating is that the efficiency of heating with an incandescent source is low. Another apparent disadvantage was discovered when full-frame heating, using an industrial heat lamp (250-watt, internal-reflector type), was tried. Intensity was varied by adjusting the lamp-to-film distance. At relatively low intensities the frost developed in approximately one minute and was comparable to platen-developed frost. At the higher intensities needed to obtain development in a few seconds, the timing was extremely critical and the maximum density was low (approximately one third of normal). It was theorized that, with rapid testing, the temperature of the film follows a rapidly rising course and that, during the heating cycle, the temperature is generally too low or too high for the total heating time involved.

In other experiments with infrared heating, the film was pulled past a one-half-inch-wide rectangular aperture collimating the radiation from a 190-watt, quartz tube infrared lamp. In this case silicone oil-coated films developed to maximum density (1 at  $f/4$ ) at a transport rate of 12 inches per minute. This corresponds to a heating time of less than three seconds. Silicone oil was used on the films because this corresponds to the most likely condition when frost is combined with charge transfer.

It is planned to study infrared heating using infrared lamps at two intensities simultaneously: a relatively low intensity sufficient to maintain a film at frosting temperature and a high-intensity lamp operated for a shorter time to quickly heat the film to the frosting temperature.

Experiments are under way to determine the latitudes in frost heating time and frost temperature.

#### c. Resistance Heating

Resistance heating in which current is passed through the conductive layer of the film substrate was briefly investigated. Three-inch-square substrates of Inconel-coated Mylar ( $1\frac{1}{2}$   $\mu$ ) were coated uniformly with Resin Compound X-2 except for two strips along opposite edges that were left uncoated. These

strips were coated with silver paint to increase the conductivity of the contact. The resistance across the strips was approximately 100 ohms. Application of approximately 50 volts caused the films to frost in a few seconds. However, the frost was erratic and nonuniform. In some cases electrical sparking could be seen on the film during heating, suggesting that breaks in the conductivity path were the cause of the spurious results. Although resistance heating has genuine advantages for some applications, it is felt that the additional limitations imposed on the frost film by the requirements for resistance heating make this approach unattractive for the present project, which is designed to demonstrate laboratory feasibility only.

#### d. Hot Gas Heating

Brief experiments were performed using an electric hair dryer to heat Mylar-supported films. With the particular unit used, the size of the heated area was approximately 1-1/4 inch square so that it was necessary to "scan" in order to completely develop a three-inch-square film. However, the heating was uniform over smaller areas, and further work is called for to determine the results when the dryer effluent is "fanned out" to develop a 70-millimeter width.

#### e. Hot Liquid Heating

Polyester-supported Resin Compound X-2 films were developed by dipping in hot fluorocarbon liquid. Frost uniformity was excellent and the liquid quickly evaporated to leave a dry film. Evaporation from the beaker containing the liquid appeared to be slight. If this method is to be considered seriously, measurements of possible resolution losses must be made.

### 2. Effect of Heat Development Time on Resolution

A preliminary test was undertaken to determine the effect of heat development time on the highest resolutions obtained by frost and by relief. These data are shown in Table VIII. The exposure and the heat development temperature were  $7 \times 10^{12}$  photons per square centimeter and 66 degrees centigrade, respectively. There is no clear-cut trend in these data, and most of the variation must be due to the variation in the charge transferred.

TABLE VIII.

RESOLUTION AS A FUNCTION OF HEATING TIME

Heating Time (sec)	Resolution ( $\mu$ p/mm)	
	Frost	Relief
20	47*	74
40	41*	obscured by frost
75	23	104
90	23	obscured by frost
120	29	obscured by frost

\*Lines poorly separated

3. Optical Density of Oil-Covered Frost

It is most convenient to leave the charge-transfer liquid on the Resin Compound X-2 films until after the frost development operation; and, in addition, it has been shown that there are sensitometric advantages in having silicone oil on the Resin Compound X-2 film during development. However, if it is required to view the film with minimum delay after heat development, it is important to know the effect of silicone oil on the viewing of the frost film. Brief experiments were therefore performed to measure the optical density of frost films, with and without oil on their surfaces. In addition, the frost density was measured on films covered with a film of silicone oil and then blotted as completely as possible with a facial tissue. Other cleaning methods are also possible, but none could be much simpler. It was found that rubbing with the facial tissue caused serious scratches and that only gentle blotting could be accomplished without film damage.

In Fig. 22, the optical densities of oil-coated films are plotted against the densities in the same areas after complete removal of the oil. Although there is extensive point scatter, it is clear that density is greatly diminished by the oil film. Densitometer traces of films coated with oil and then blotted

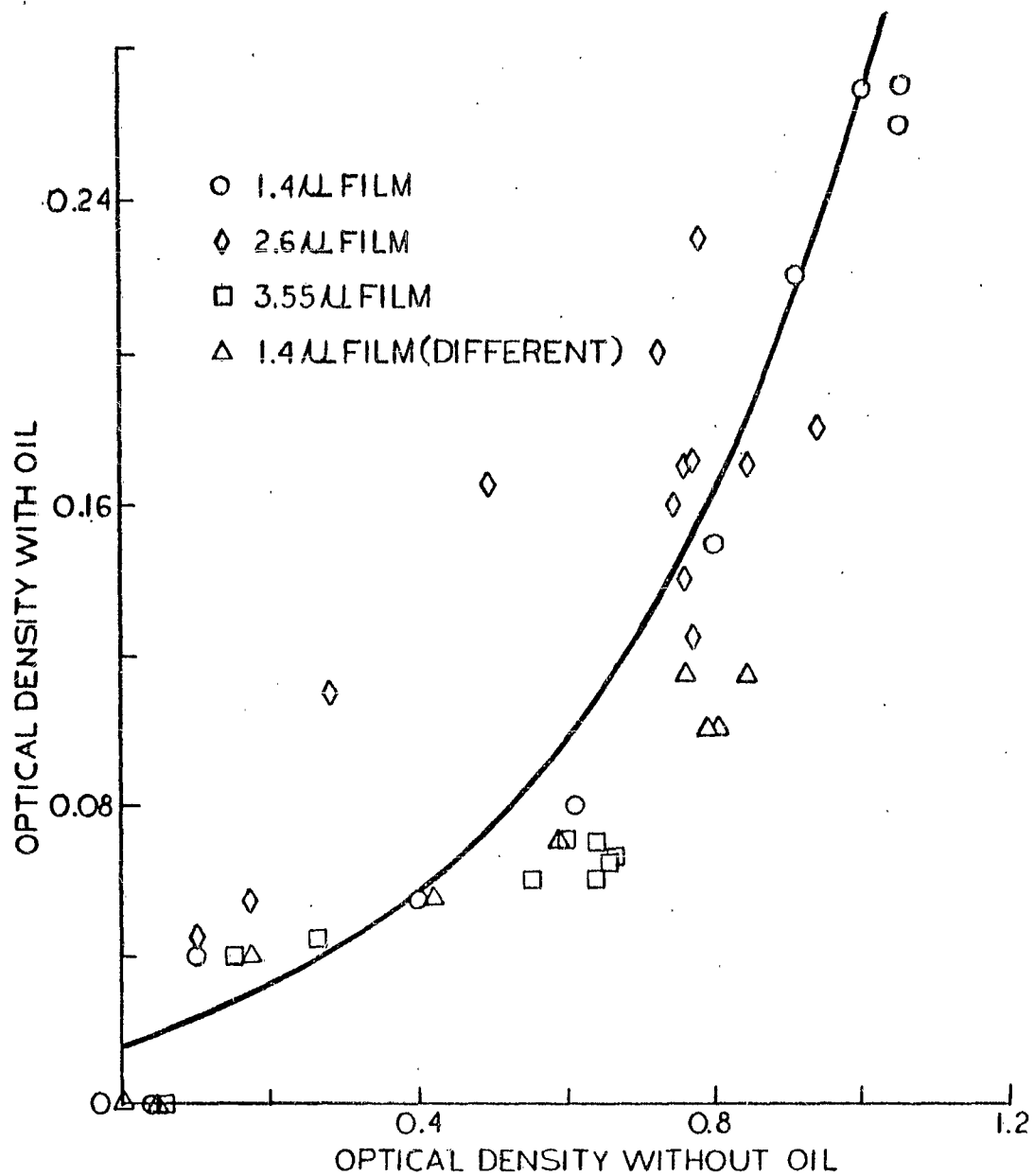


FIGURE 22. Effect of Silicone Oil on Frost Density

were indistinguishable from those of unblotted oil films, although slight differences could be seen by visual examination.

#### 4. "Wet" vs. "Dry" Heat Development

As discussed above, fluorocarbon liquids can be used for charge transfer. These materials have higher vapor pressures and lower viscosities than the silicone fluids that can be used in conjunction with Resin Compound X-2. The fluorocarbon liquids evaporate so readily that immediate viewing is possible without a cleaning step. The main disadvantage of such materials is that frost development must be performed "dry," after the liquid has evaporated. Evaporation is so rapid that little or no delay is involved, but charge densities must be considerably higher. Table IX lists approximate potential levels required for two-micron Resin Compound X-2 films developed with and without a layer of silicone fluid.

TABLE IX.

POTENTIAL IN VOLTS REQUIRED FOR  
"WET" AND "DRY" DEVELOPMENT OF 2  $\mu$  FILMS

	<u>V<sub>shoulder</sub></u>	<u>V<sub>toe</sub></u>
Silicone-fluid-coated	60	30
No silicone fluid	160	110

In addition to the present difficulty of obtaining potentials as high as 160 volts on the electrode, it is believed that the heat development time of the dry films is more critical. Further study is required to determine whether "wet" or "dry" development is preferred.

#### 5. Uniform Charging for Sensitometric Purposes

It was pointed out in the previous report that there may be advantages in applying a uniform charge to the charge-receiving layer. The image charge can be added to or subtracted from this uniform charge prior to frost development. Such a system allows some manipulation of the photographic characteristic curve, and in addition, increases system sensitivity.

In the case of "wet" development, the charge levels are low enough that the uniform charge can be obtained by the charge-transfer technique. Our usual practice has been to apply, while the room lights are on, an external potential of a value somewhat higher than the value of uniform potential desired. The lights are then extinguished and the image exposure is made in the usual way. In a typical charge subtraction experiment, Liquid 34 was used with applied potentials of -200 and +400 volts (polarity of the film substrate) for the uniform and image exposures, respectively. Fair to good continuous-tone images were made by this technique.

For the high potentials required for "dry" development, fluorocarbon Liquid 50 was employed. It was not possible to precharge the resin film to a sufficiently high potential by charge-transfer techniques, and so corona charging was substituted. Using this technique, excellent images were prepared. Continuous-tone and line-copy images required exposures at the photoconductor of approximately  $2 \times 10^{12}$  and  $7 \times 10^{12}$  photons/cm<sup>2</sup>, respectively (measured with the original transparency removed).

The charge subtraction imaging mode suffers from one difficulty that has not yet been completely evaluated. When the polarity of the external potential is reversed prior to the image exposure, charge is removed from the resin layer. This effort is evidently due to a combination of relaxation of polarization charge in the liquid and dark current or "sweep-out current" in the photoconductor. The effect of this charge loss is to require a considerably larger precharge potential than is finally required. This effect may constitute a serious disadvantage of charge-subtraction operation.

#### 6. Full-Size Imaging Tests

Most of the images prepared until recently have been made in conjunction with the high-resolution camera which is capable of exposing areas no larger than approximately eight millimeters square. More recently the prototype camera-developer device has been used to produce full-size (2-in. square) images. Valuable experience has been gained in methods of contacting the film and photoconductor with an intervening liquid layer and in determining the effects of dust contamination on image quality. In addition, this device has been used for imaging tests with the panchromatic photoconductor.

Of the various means for contacting the electrode film to the selenium plate, a modified squeegee (similar to the devices used for window washing) was found to be most effective. It was found that most of the spots and voids in the frost image caused by incomplete charge transfer could be avoided by applying an excess of the charge-transfer liquid and forcing out the excess during film application. Dust particles cause "tenting" of the film on the photoconductor, which causes areas of reduced charge-transfer. Much further work is required to find means for entirely eliminating image defects.

#### 7. "In-Place" Development

In a brief exploratory experiment an image was produced by "in-place development," i.e., by leaving the film in contact with the selenium plate after charge transfer, heating the sandwich on a hot plate until an image appeared, and then stripping the film from the plate. In the one trial, it was found that part of the deformable resin was stripped from the film and was left on the plate. This technique might have some advantages, but the problems of heat development are considered formidable and no further experiments are planned for the current project. This technique, however, might be considered in the future as a variation of charge-transfer-frost, which would avoid the problems of rapid transport to a heat development station.

## V. MATERIALS

### A. INTRODUCTION

Studies in this section pertain to the selection and fabrication of all materials for the camera-developer device with the exception of the photoconductor. This includes finding the best materials for the deformable film, the conductive layer, the base layer, and the charge-transfer liquid. Engineering effort to devise means for fabricating high-quality multiple-layer films in larger quantities constitutes the second important phase of this work.

### B. THERMOPLASTIC LAYER

As stated in the previous interim report <sup>5</sup>, Resin Compounds X-1, X-2, and X-3 all have the resistivity and viscosity characteristics required for deformation. Resin Compound X-2 gives the highest frost image densities and is not appreciably affected by the charge-transfer liquids presently used. However, its frost properties change on aging because of oxidative attack upon reactive positions. Resin Compound X-3, the hydrogenated derivative of X-2, is stable because it contains no unsaturation. However, it is at least slightly soluble in the charge-transfer liquid. A second derivative of Resin Compound X-2 was obtained with a degree of hydrogenation between those of X-2 and X-3. As might have been expected, this material, X-4, also has an intermediate melting point, solubility, stability, and frost density. It might be a suitable thermoplastic to use if Resin Compounds X-2 and X-3 later prove to be borderline in any of these properties.

A preliminary evaluation of another thermoplastic, Resin Compound X-5, was completed. The softening temperature of this material is 40°C higher than that of Resin Compound X-2. The frost density seems equally good. However, unless difficulties are experienced with Resin Compounds X-2 or X-3, extensive tests of Resin Compound X-5 do not appear to be justified. This material will be regarded for the time being as an alternative material to be held in reserve. It will be tested further if unexpected problems arise. One such problem is the recent difficulty encountered in attempts to coat Resin Compound X-2 on a pilot plant scale (See Section V-F). If these difficulties cannot be overcome, a more extensive evaluation of Resin Compound X-5 will be made. However, the similarity of all frostable materials so far known suggests that coating problems may be severe for any of these materials presently available.



## C. CHARGE-TRANSFER LIQUID

### 1. Requirements

The first requirement of a charge-transfer liquid is that it have negligible solvent effect upon the thermoplastic layer. Since the frostable thermoplastics are generally very soluble, even in hydrocarbons, this means that the charge-transfer liquid must be exceptionally inert. Secondly, the charge-transfer liquid must be conductive enough to transfer the required amount of charge from the photoconductor to the thermoplastic in a short time, yet not so conductive that lateral spreading or loss of charge occurs before development. Because the precise conductivity required varies with imaging conditions, the conductivity requirement is best satisfied by a liquid which when pure is less conductive than required, but which can be adjusted to a range of higher conductivities by means of doping agents.

### 2. Testing

A simple means of measuring the conductivity of charge-transfer liquids is not yet available. Screening tests were made by measuring the potential acquired by a thermoplastic-coated electrode after a charge-transfer operation. Differences in the potentials measured depend upon "short" times; \* but, with the durations used, higher potentials indicate liquids of higher conductivity.

### 3. Silicone Fluids

The first liquids tested which met the requirements given were the polysiloxane fluids. Four types were tested, alone and with the following doping agents:

1. Water
2. Two metal salts
3. Six different liquid polymers
4. A commercial antistatic agent
5. Seven metallic soaps
6. Three organometal compounds
7. Three silicone chemicals

Some typical charge-transfer results for several liquids are given in Table X. Most of the above materials were not effective dopants because of insolubility in silicone oil, but fairly good charge-transfer results were finally obtained with two organometal compounds present in Liquids 21 and 34. Comparative data on the charge-transfer ability of these two liquids under one set of conditions are included in Table XI. The electrode potential obtained

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\* See Section IV-B-3.

TABLE X.

## CHARGE-TRANSFER TESTS OF VARIOUS LIQUIDS\*

Liquid No.	Composition	Average Electrode Potential (V exposed -V background) Electrode+ Electrode-
24	Silicone Liquid 3	-12, -8, -7
25	Silicone 2	14, 0
26	Silicone Liquid 1 + Metallic Soap 1	0, 0
27	Silicone Liquid 1 + Metallic Soap 2	0, 0
28	Silicone Liquid 1 + Metallic Soap 3	0, 0
29	Silicone Liquid 1 + Metallic Soap 4	0, 0
30	Silicone Liquid 1 + Metallic Soap 5	0, 0
31	Silicone Liquid 1 + Metallic Soap 6	0, 0
32	Silicone Liquid 1 + Metallic Soap 7	0, 0
33	Silicone Liquid 1 + Organometal 1	0, 0
34	Silicone Liquid 1 + Organometal 2	0, 0
35	Silicone Liquid 1 + Silicone A	0, 0
36	Silicone Liquid 1 + Silicone B	0, 0
37	Silicone Liquid 1 + Silicone Liquid 19, 2:1	0, 0
38	Silicone Liquid 1 + Silicone Liquid 19, 1:1	0, 0
39	Silicone Liquid 1 + Silicone Liquid 19, 1:2	0, 0
--	Octoil	0, 0

\*Conditions: 1/2-sec. exposure ( $10^{12}$  photons/cm<sup>2</sup>/sec. at 4000Å)

5-sec. short period

400 volts external potential

2-micron Resin Compound X-6 layers

XEROX

with Liquid 34 is about twice that obtained with Liquid 21, indicating a higher conductivity for the former. The use of pure silicone oil usually results in no measurable potential under the these conditions.

A second type of silicone oil is supplied commercially in two grades, one (Liquid 18) pure and one (Liquid 19) containing a rust inhibitor. The one containing rust inhibitor was found to be more conductive, as shown in Table XI. Data for Liquid 34, under the same conditions, are included for comparison.

TABLE XI.

CHARGE-TRANSFER TESTS OF LIQUIDS 18 and 19\*

Liquid	Electrode Polarity	Average Electrode Potential ( $V_{\text{exposed}} - V_{\text{background}}$ ) (volts)
34	-	44.28
	+	-22
18	-	0
	+	-6
19	-	+8
	+	-24

\*Conditions: 1/2-sec. exposure ( $10^{12}$  photons/cm<sup>2</sup>/sec. at 4000Å)  
 5-sec. short period  
 400 volts external potential  
 2-micron Resin Compound X-6 layers

4. Fluorocarbon Liquids

The second class of inert liquids to be tested were the completely fluorinated organic chemicals. These are of particular interest because they evaporate readily and the image requires no cleaning. They were found to be even more inert than the silicone oils, i.e., having more limited solvent action on most

materials, including the thermoplastics and possible doping agents. However, one doping agent was found with which three different fluorocarbons could be made as conductive for charges of negative polarity as Liquid 34. Test data are given in Table VII, Section IV-B-5.

#### D. CONDUCTIVE LAYER

Evaporated films of copper iodide, copper, silver, gold, aluminum, chromium and Inconel were prepared and evaluated for resistivity, transparency, age stability, adhesion to substrate, and compatibility with the deformable layer. The best optical transmission for usable resistances (one megohm per square or less) was found for chromium and Inconel. Copper and aluminum films were unstable; their resistances increased with time. Gold and silver did not adhere well to Mylar; and, in addition, the ratio of resistance to transmission was erratic. These films were overcoated with Resin Compound X-2, oven dried, and frosted. The gold films became nonconductive during baking. The silver films developed only low-density wavy frost patterns. The copper iodide films gave erratic results (believed to be due to a reaction with Resin Compound X-2). The chromium and Inconel films alone gave good frost.

More recently, some samples of aluminum-coated Mylar were obtained from a commercial firm. These combined satisfactory light transmission (66%) with high electrical conductivities (500 ohms/square) and were superior to the aluminum coatings previously made at Xerox. A 4000-foot roll was then ordered and evaluated. Optical transmission and resistance per square were approximately 60% and 5000 ohms, respectively, and varied across the web. The aluminum coating was somewhat too variable in thickness for the final product but should serve well for coating trials.

#### E. FILM BASE

The requirements of the film base are that it be smooth, transparent, flexible, and heat and solvent resistant. Lexan\* and polyester films were examined. Lexan films were too rough to use and some types of Mylar film were quite hazy. Optical-quality polyester films from two sources appear to be satisfactory.

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\*General Electric Company

## F. COMPLETE FILM MANUFACTURE

Until fairly recently coating trials using roll-coating equipment have not been possible for lack of a sufficient quantity of the base material in continuous lengths. When the 4000-foot roll of the material mentioned became available, this situation was alleviated. Two pilot plant coating trials have been run with the above-mentioned base and Resin Compound X-2 on a reverse-roll coater. These runs did not yield a suitable product, but they did point out the difficulties of coating Resin Compound X-2. These difficulties are:

1. Resin Compound X-2 has a "shallow" viscosity-vs.-concentration curve. Accurate metering of coating thickness and width is thus difficult on a roll coater. The wet coating also has a tendency to run before it can be "set" by oven-drying.
2. Drying problems have been encountered with Resin Compound X-2. Because of the short time the film is in the oven, the drying air temperature must be in the 300°F range. This temperature is too low to remove all solvent, and it is feared that higher temperatures may result in deterioration in frost properties. (This has been observed in the laboratory.)
3. The Resin Compound X-2 layer prepared by roll coating has shown poor handling characteristics after drying. The film appears to be very brittle and cracks when the film is bent or creased.
4. The coated film cannot be rewound without severe blocking (sticking to the back of the next wrap). Teflon interleaving, although helpful, has not eliminated this defect.
5. During coating both the wet and dry layers readily pick up dust particles that cannot be successfully removed.

Our present understanding of the causes of these difficulties are listed in the same order below, along with possible solutions.

1. Viscosity. Non-viscous solutions may be applied more effectively by gravure roll applicators. This method is excellent for accurate control of coating weight and registration. Also, additives will be examined as "thickening" agents.
2. Drying. Higher oven temperatures may help, but if normal drying techniques prove to be unsatisfactory, a tunnel dryer (similar to those used in the photographic industry) or an infrared dryer may be satisfactory.

3. Handling. There are two possible reasons why the Resin Compound X-2 coating has such poor handling characteristics. The first is that wetting of the base is poor, and the second is that the coating is naturally a nonflexible, glass-like coating. If poor wetting of the base is the main cause of shattering, wetting agents will be used prior to coating. However if the origin of "shattering" is in the inelastic film-forming characteristics of Resin Compound X-2, a new material or modification of the existing material may be required. It is also planned to substitute a thicker (3-mil instead of 1-1/2-mil) polyester base to lessen creasing.

4. Blocking. Blocking tendencies may be diminished by more adequate drying. There may be some possibility of reducing blocking by using release agents.

5. Dust. The solution to the dust problem is best resolved by coating in a photographically clean coating area.

As a stand-by while the roll-coating operation was studied, other coating techniques were investigated. The most successful of these is a draw-down technique using a gravure applicator. This method gives coatings superior to those made on the reverse-roll coater. Quality is adequate for present laboratory use.

Spray coating was also tried as a technique for applying Resin Compound X-2. Like the draw-down technique, this method has the advantage of being able to use short lengths of base material. However, coating uniformity is inferior to that obtained by gravure draw-down.

## VI. CAMERA-DEVELOPER DEVICE

A working model of the camera-developer device, as described in Interim Engineering Report No. 1,<sup>5</sup> has been constructed and successfully employed in the evaluation of the process of forming full-sized images. However, research studies during the period resulted in the formation of a revised set of requirements for the basic process which indicated limited usefulness of this initial hardware. The new process requirements stem from our improved understanding of the characteristics of the charge-transfer process. Because the lateral conductivity of efficient charge-transfer liquids is not negligible, improved resolution should result from reduction of the period between formation of the electrostatic image and frost development. Consequently, the decision was made early in the period to relegate this first device to preliminary studies and support the process with a new machine concept based on these new requirements, while, as before, recognizing the intent of the contract work statement to minimize hardware sophistication.

Re-evaluation of the camera-developer device on this basis resulted in the following decisions:

1. The basic device is a camera for holding lens and imaging materials in the necessary orientations and intervals. Other process steps offer alternatives regarding where and when they must be accomplished. In the early work on the project, it was felt that processing within the camera box itself would, in general, necessitate more mechanism and complexity and thus more engineering than if these functions were accomplished externally "on the bench" where human dexterity can be effectively substituted for mechanism. However, the new requirement for minimizing the delay between exposure and development suggested the need for transport speeds and repeatability of process steps that would be in excess of human capabilities. Therefore, in this context, separation of the image-bearing film from the photoconductor, transporting to a heat-development station, and development can best be accomplished within the camera device. It is planned that all other process steps will be accomplished in the peripheral equipment.

2. A swinging frame offers the simplest configuration for film separation and transport. This form of mechanism assures a less complex configuration when the film is used in pre-cut sheets rather than a roll format, and, since viewing in any event would not be from the roll, film chips will be employed in the new device. Materials sufficient for the formation of a single image will be loaded in the device prior to each usage.

3. The redesigned camera will be set up to use the GFE\* lens at a 7:1 object-to-image ratio, with provision to extend this to 50:1 for better image quality, when needed. Adjustment for critical focus and optical alignment will also be provided. Actual image size will be 2 x 2 inches on a 70-mm-wide film.

4. Formation of the liquid layer between film and photoconductor will be accomplished prior to loading materials into camera. Laboratory attempts to coat either the photoconductor or the electrode, or both, with a thin film of charge-transfer liquid prior to assembly were unsuccessful because of the entrainment of air between the films. This problem is overcome when the film is applied with a bead of fluid. The film is squeegeed into position and the excess liquid is spread and removed by successive passes of a wiper. This technique has produced suitable liquid layers with respect to thickness, repeatability, and absence of defects.

5. Film separation after exposure and before development has been examined in sufficient detail to assure us that a component of force in the plane of the photoconductor of sufficient magnitude to induce slippage, and image smear is highly unlikely. This is expected to be true for all the mechanisms under consideration for this process step. Actual peeling will require 0.1 second or less.

6. A survey study of the basic alternatives for application of heat for development has been completed. Radiant heating or heating with hot gas are preferred because physical contact need not to be made with the film. Initially, we will work with the former since this appears to offer the most desirable set of characteristics for use in a simple image-forming device. Work is currently under way to examine this method in depth and develop the specific process that will be employed.

Various possible mechanisms for the camera-developer device have been studied. Sketches of some kinematic arrangements have been evaluated for complexity, reliability and compatibility with process requirements. Better understanding of process steps has provided a basis for this study.

A suitable method for contacting the film and photoconductor through a reproducible oil film of uniform thickness has been worked out and is in process of detailed design.

Major effort at present is devoted to heat development methods. As a result of laboratory tests, several inferior methods have been discarded. Further work is in progress to determine the best technique. At the conclusion of this work, the major processing steps will be fully determined and the design can proceed to the detail level.

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\* Supplied by the Air Force.



## VII. CONCLUSIONS

Based on the results of the first 12 month's effort, the following tentative conclusions can be drawn:

1. Problems with charge transfer through liquid layers have required more effort than anticipated, and have necessitated a basic revision of the camera-developer device. Manufacture of the complete deformable film is also more difficult than anticipated. With these exceptions, each phase of the program has progressed satisfactorily and is on schedule.

2. Tests of the rear exposure panchromatic photoconductor, although preliminary, are gratifying as regards uniformity. The objective of an ASA exposure index of 10 to 12 seems attainable by the presently contemplated system. Preparative repeatability so far appears adequate.

3. The nature of the liquid charge-transfer process necessitates a compromise between resolution and charge-transfer completeness. The latter must be kept high not only to maintain the photographic sensitivity, but also to give adequate image uniformity. The possible resolution loss resulting from high-conductivity charge-transfer liquids will be reduced by rapid film transport between photoconductor and the development station. It is not yet known what resolutions can be achieved at high charge-transfer efficiency. Approximately 40 line pairs/millimeter have been achieved thus far; resolutions of 70 to 100 line pairs per millimeter appear difficult but possible.

4. Continuous-tone response of frost images appears adequate, but processing conditions are still being worked out.

5. Several deformable materials have been found which seem adequate to demonstrate frost imaging, but serious fabrication problems remain because of the poor film-forming characteristics of these materials.

6. A range of conductivities can be obtained in charge-transfer liquids by doping. Either evaporable or non-evaporable liquids can be provided.

7. The simple camera-developer device was built and used for tests, but a redesign was found necessary to circumvent unforeseen difficulties with the charge-transfer process. This is under way.

## VIII. FUTURE PLANS

The following plans seem consistent with the present status of our technical work.

### A. PHOTORECEPTOR

It is assumed that the present rear-exposure selenium-tellurium panchromatic plate will meet the requirements of the project, perhaps with minor changes in the control layer thickness or composition to take advantage of the relatively short pulse times. Concentrate on uniformity tests in the total system and any remaining manufacturing problems.

### B. METHODS

Decide between evaporable and non-evaporable charge-transfer liquids. Determine sensitometric characteristics of total system and optimum operating conditions.

### C. MATERIALS

Investigate means of improving film manufacture to prevent present blocking and cracking problems. Obtain source of better quality conductive substrate material.

### D. CAMERA-DEVELOPER DEVICE

Continue redesign of camera-developer device to allow for rapid film transport between the photoconductor and the heat development section. Utilize this device to find optimum operating conditions, to provide samples, and to demonstrate the process.

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